

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

**APPENDICES**

**FOR THE**

Report for the Application (Del Norte County)  
and Ambient (Fresno County) Air Monitoring  
of Phorate

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C97-040 (Application)  
C97-002 (Ambient)

Date: November 13, 1998

APPENDIX I  
SAMPLING PROTOCOL



**Cal/EPA**

California  
Environmental  
Protection  
Agency



**Air Resources Board**

P.O. Box 2815  
2020 L Street  
Sacramento, CA  
95812-2815


**MEMORANDUM**



**Pete Wilson**  
Governor

**James M. Strock**  
Secretary for  
Environmental  
Protection

**TO:** John S. Sanders, Ph.D., Chief  
Environmental Monitoring and Pest  
Management Branch  
Department of Pesticide Regulation

**FROM:** George Lew, Chief   
Engineering and Laboratory Branch

**DATE:** March 17, 1997

**SUBJECT:** FINAL PROTOCOL FOR THE 1997 PHORATE AMBIENT MONITORING  
IN FRESNO COUNTY

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Enclosed is the final protocol, "Protocol for the Ambient Air Monitoring of  
Phorate in Fresno County During April, 1997."

If you or your staff have questions or need further information, please contact  
me at (916) 263-1630 or Mr. Kevin Mongar at (916) 263-2063.

Enclosure

**cc:** Ray Menebroker, Chief (w/Enclosure)  
Project Assessment Branch  
Stationary Source Division

**bcc:** Bill Loscutoff, MLD  
Peter Venturini, SSD  
Don Ames, SSD  
Mike Tollstrup, SSD  
Lynn Baker, SSD  
Doug Edwards, FC Ag. Comm. Office  
David Crow, SJVUAPCD

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

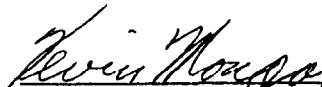
Protocol for the Ambient Air Monitoring  
of Phorate  
In Fresno County During April, 1997


Engineering and Laboratory Branch  
Monitoring and Laboratory Division

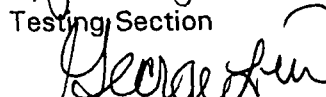
Project No. C97-002

Date: March 14, 1997

APPROVED:

  
Kevin Mongar, Project Engineer

  
Cynthia L. Castronovo, Manager  
Testing Section

  
George Lew, Chief  
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for the Ambient Air Monitoring  
of Phorate  
In Fresno County During April, 1997

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), (February 27, 1997 Memorandum from John Sanders to George Lew) the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide phorate O,O-Diethyl S-ethylmercaptomethyl dithiophosphonate (phorate) over a six week ambient monitoring program in areas frequented by people. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The monitoring program will be conducted in Fresno County.

The draft method development results and "Standard Operating Procedures for the Analysis of Phorate in Ambient Air" (contracted to the University of California, Davis (UCD)) are not included in this protocol but will be included in the draft report.

II. Chemical Properties of Phorate

Phorate (CAS: 298-02-2) exists as clear liquid. Phorate has a molecular formula of  $C_7H_{17}O_2PS_3$  a formula weight of 260.40 g/mole, and a specific density of 1.156 at 25/4 °C. Phorate has a water solubility of 20 mg/L at 24 °C, a Henry's Constant of  $6.4 \times 10^{-6}$  atm·m<sup>3</sup>/mol at 20-24 °C, and a vapor pressure of  $8.4 \times 10^{-4}$  mm Hg at 20 °C. Phorate is miscible with carbon tetrachloride, vegetable oils, xylene and various other organic solvents. The half-life ( $t_{1/2}$ ) of phorate is 96 hours at 25 °C and pH 7.0.

Phorate sulfoxide and phorate sulfone, and their phosphorothioate analogs are the major soil metabolites. Phorate sulfoxide, a microbial metabolite, may be further degraded to phorate oxon by soil-microorganisms. Purportedly, soil-type plays a larger role in phorate degradation than soil temperature or pH. Reported half-lives of phorate in loam or sandy soils are 82 days and 68 days respectively.

Exposure limits for phorate are: ACGIH TLV:TWA 0.05 mg/m<sup>3</sup> ppm, STEL 0.2mg/m<sup>3</sup>. Phorate's acute oral LD<sub>50</sub> for male and female rats is 3.7 and 1.6 mg/kg for rats. Its LC<sub>50</sub> (48 hour) is 5.4 ug/L for rainbow trout, and 1.8 ug/L for bluegill sunfish. Based on its low NOEL, phorate entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984).

III. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The resin holders are 4-3/4" long x 1-55/66" O.D. and made of Teflon. Each holder should contain approximately 30cc of specially prepared XAD-4 resin. The resin will be held in place by stainless steel screens on each side of the resin and between the Teflon support

rings. The flow rate will be accurately measured and the sampling system operated continuously with the exact operating interval noted. The resin holders will be covered with aluminum foil and supported about 1.5 meters above the ground during the sampling period. At the end of each sampling period the holders will be capped and placed in a zip-lock plastic bag with an identification label affixed. Any phorate present in the sampled ambient air will be captured by the XAD-2 adsorbent. Subsequent to sampling, the sample cartridges will be transported on dry ice, as soon as reasonably possible, to the Department of Environmental Toxicology, University of California, Davis laboratory for analysis. The samples will be stored in the freezer (-20 C) or analyzed immediately.

A sketch of the sampling apparatus is shown in Attachment A. Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data.

### Ambient Monitoring

The historical trends in phorate use suggest that monitoring should occur over a 30- to 45-day sampling period in Tulare County or Fresno County from late March through early May, with the bulk of the sampling conducted in April. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be located near cotton growing areas. Ambient samples should not be collected from samplers immediately adjacent to fields or orchards where phorate is being applied. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to phorate applications.

Replicate (collocated) samples are needed for five dates at each sampling location. Two collocated samplers (in addition to the primary sampler) should be run on those days. The dates chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling.

Four sampling sites plus an urban background site were selected by ARB personnel from the areas of Fresno County where cotton farming is predominant. Sites were selected for their proximity to the cotton fields with considerations for both accessibility and security of the sampling equipment. The five sites were at the following locations: Addresses for the sites are listed in Table 1.

TABLE 1. Ambient Sampling Sites		
BUR	Burrell Elementary School 16704 South Jameson Burrell, CA 93607	(209) 866-5634 Mildred Wylie Principal
ARB	Air Resources Board, Ambient Air Monitoring Station 3425 N First, Suite 205B Fresno, CA 228-1825	(209) 228-1825
FP	Westside Elementary School 19191 Excelsior Ave. Five Points, CA 93624	(209) 884-2492 Baldomero Hernandez Principal
SJ	San Joaquin Elementary School 8535 South 9th San Joaquin, CA 93660	(209) 693-4321 Jackie Newman Principal
HEL	Helm Elementary School 13883 S. Lassen Avenue Helm, CA 93627	(209) 866-5683 Sylvia Grider Principal

The samples will be collected by ARB personnel over a six week period from March 24 - May 2, 1997. 24-hour samples will be taken Monday through Friday (4 samples/week) at a flow rate of 15 L/minute.

#### IV. Analysis

The method development results and "Standard Operating Procedures for the Analysis of Phorate in Ambient Air" are not included in this protocol but will be included in the draft report.

#### V. Quality Assurance

Field Quality Control for the ambient monitoring will include:

- 1) Five field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling), spiked at five different levels. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 15 L/minute.
- 2) Five trip spikes will be prepared and spiked at five different levels.
- 3) Replicate samples will be taken for six dates at each sampling location.

- 4) Trip blanks will be obtained at each of the five sampling locations.

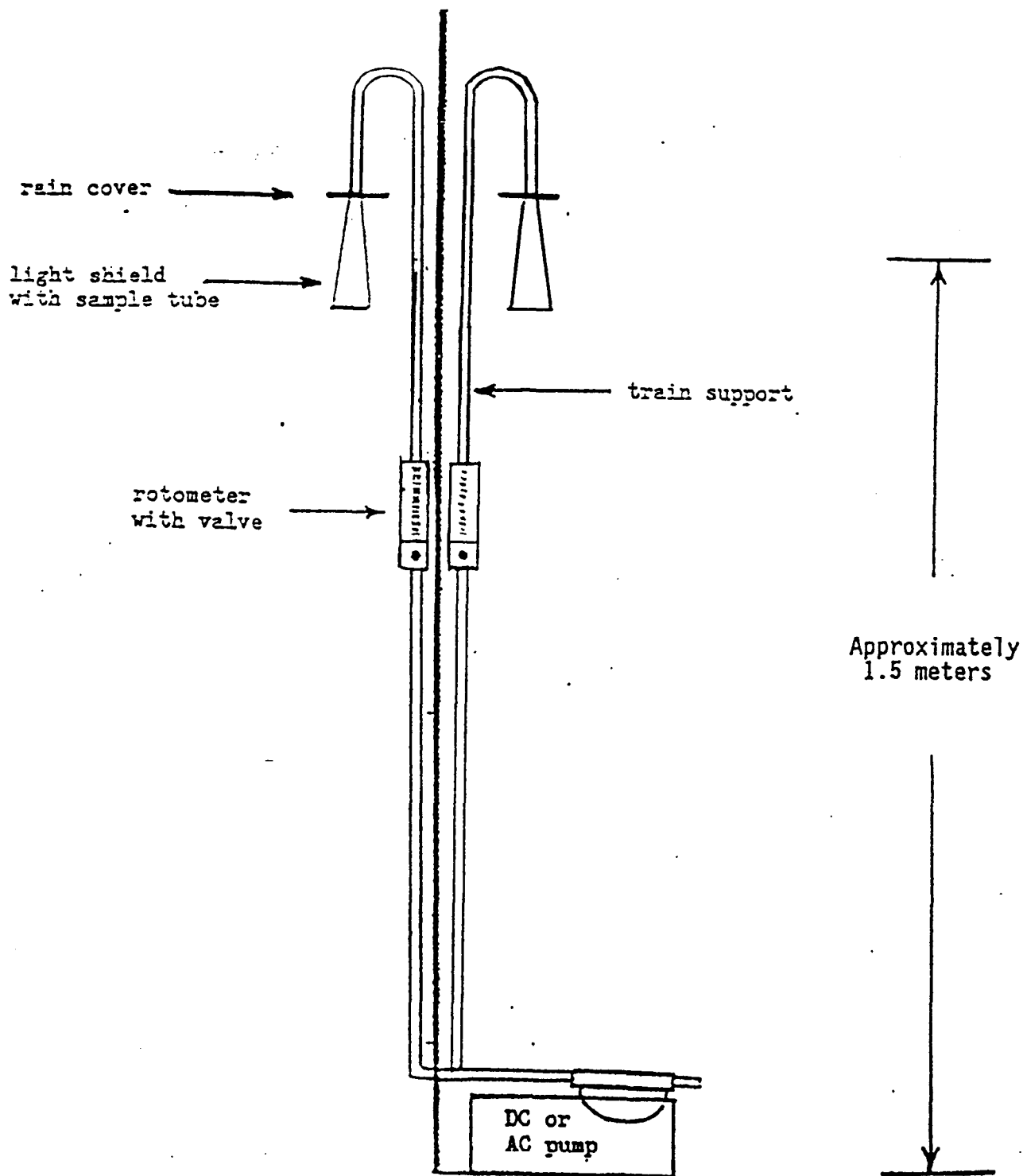
A chain of custody sheet will accompany all samples. Rotameters will be calibrated prior to and after sampling in the field.

VI. Personnel

ARB personnel will consist of Kevin Mongar (Project Engineer) and an Instrument Technician.



**Attachment A**





Cal/EPA

California  
Environmental  
Protection  
Agency



Air Resources Board

P.O. Box 2815  
2020 L Street  
Sacramento, CA  
95812-2815


# MEMORANDUM



Pete Wilson  
Governor

~~XXXXXXXXXX~~  
Secretary for  
Environmental  
Protection

TO: John S. Sanders, Ph.D., Chief  
Environmental Monitoring and Pest  
Management Branch  
Department of Pesticide Regulation

FROM: George Lew, Chief   
Engineering and Laboratory Branch

DATE: August 20, 1997

SUBJECT: PROTOCOL FOR THE 1997 PHORATE APPLICATION MONITORING IN  
DEL NORTE COUNTY

Enclosed is the final protocol, "Protocol for the Application Air Monitoring of Phorate in Del Norte County." Monitoring will occur this summer or fall (tentatively scheduled for the week of August 24, 1997) as suggested in your February 1997 memorandum.

If you or your staff have questions, please contact me at (916) 263-1630 or Mr. Kevin Mongar at (916) 263-2063.

## Enclosure

cc: Ray Menebroker, SSD  
Glenn Anderson, Del Norte Co. Ag. Comm. Office  
Wayne Morgan, North Coast Unified AQMD

bcc: Bill Loscutoff, MLD  
Peter Venturini, SSD  
Lynn Baker, SSD

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

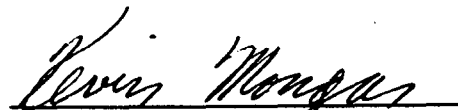
Protocol for the Application Monitoring  
of Phorate  
In Del Norte County

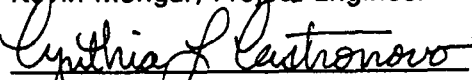
Engineering and Laboratory Branch  
Monitoring and Laboratory Division

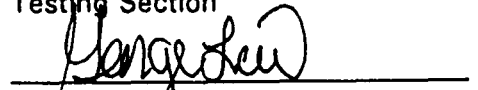
Project No. C97-040

Date: August 15, 1997

APPROVED:

  
Kevin Mongar, Project Engineer

  
Cynthia L. Castronovo, Manager  
Testing Section

  
George Lew, Chief  
Engineering and Laboratory Branch

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Protocol for the Application Monitoring  
of Phorate  
In Del Norte County

I. Introduction

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The draft method development results and "Standard Operating Procedures for the Analysis of Phorate in Ambient Air" (contracted to the University of California, Davis (UCD)) are included as Attachment B.

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rings. The flow rate will be accurately measured and the sampling system operated continuously with the exact operating interval noted. The resin holders will be covered with aluminum foil and supported about 1.5 meters above the ground during the sampling period. At the end of each sampling period the holders will be capped and placed in a zip-lock plastic bag with an identification label affixed. Any phorate present in the sampled ambient air will be captured by the XAD-4 adsorbent. Subsequent to sampling, the sample cartridges will be transported on dry ice, as soon as reasonably possible, to the Department of Environmental Toxicology, University of California, Davis laboratory for analysis. The samples will be stored in the freezer (-20 C) or analyzed immediately.

A sketch of the sampling apparatus is shown in Attachment A. Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data.

#### IV. Application-Site Air Monitoring

The historical trends in phorate use suggest that application-site air monitoring should be conducted during August, September, or October in Del Norte County where application rates are consistently high. Application rates to nursery commodities (cut flowers, field grown plants, etc.) range from 8.1 lbs AI/acre to 9.5 lbs AI/acre. Although phorate is not widely applied in Del Norte County during these months, care should still be taken so that nearby applications do not contaminate collected samples. A three day monitoring period should be established with sampling times as follows: application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of five samplers should be positioned, one on each side of the field, the fifth sampler should be collocated at one position. Background samplers should collect enough volume (either 12 hours at 15 liters/min., or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally, samplers should be placed a minimum of 20 meters from the field, however, wherever samplers are placed, the distance from the field must be reported. Field spike samples should be collected at the same environmental conditions (temperature humidity, exposure to sunlight) and experimental conditions (similar air flow rates) as those occurring at the time of sampling.

Additionally, we will provide in the monitoring report: 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover; and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North).

The specific location of the application monitoring will be determined after communication and close coordination with the Del Norte County Agricultural Commissioner's Office.

## **V. Analysis**

The method development results and "Standard Operating Procedures for the Analysis of Phorate in Ambient Air" are included in this protocol as attachment B.

## **VI. Quality Assurance**

Field Quality Control for the application monitoring will include:

- 1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air during the site background monitoring.
- 2) Four trip spikes.
- 3) Replicate samples will be taken for all samples at one sampling location.
- 4) A trip blank will be obtained.

A chain of custody sheet will accompany all samples. Rotameters will be calibrated prior to and after sampling in the field. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data.

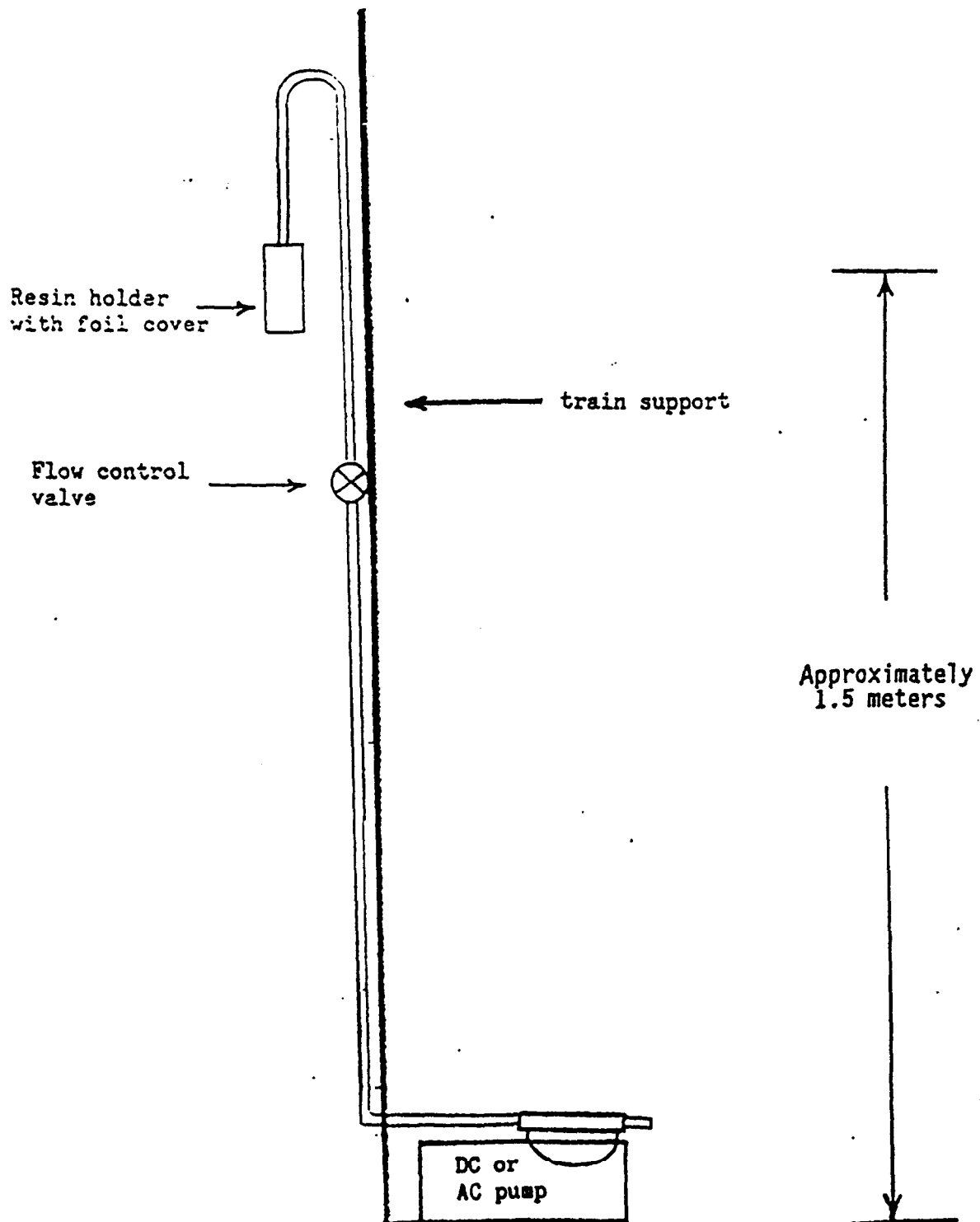
## **VII. Personnel**

ARB personnel will consist of Kevin Mongar (Project Engineer) and two Instrument Technicians.

**Attachment A**



FIGURE 1  
FIELD SAMPLING APPARATUS



**Attachment B**

## **Standard Operating Procedure for the Analysis of Phorate in Ambient Air**

### **1. SCOPE**

The method utilized is a gas chromatographic method with a flame photometric detector (FPD) and a 526 nm filter that is selective for phosphorus compounds. This method has been used by Environmental Toxicology personnel for the analysis of organophosphates in air.

### **2. SUMMARY OF METHOD**

Exposed XAD-4® resin samples are stored either in an ice chest with dry ice or at -20 °C in a freezer. Samples are extracted with 75 mL of ethyl acetate and an aliquot is oxidized with potassium permanganate to phorate sulfone and phorate oxon sulfone, then concentrated prior to injecting 3 µL on to a gas chromatograph equipped with a flame photometric detector. Results of both compounds are mathematically converted back to parent compound and reported as total phorate.

### **3. INTERFERENCES/LIMITATIONS**

Potential interferences may arise due to contaminants in laboratory solvents, reagents, glassware and/or apparatus. A reagent blank and/or control resin blank must be run through the method procedure and analyzed with each set of samples. We reserve the right to change this standard operating procedure should the need arise to handle unforeseen complications with the compounds of interest.

### **4. EQUIPMENT AND CONDITIONS**

#### **A. Instrumentation**

Hewlett-Packard 5890 Series II gas chromatograph  
Hewlett-Packard 7673 Autosampler  
Perkin-Elmer TurboChrom® Data System  
Microsoft Excel®, version 7.0

Injector : 250°C

Detector: 225°C

Column: Restek XTI-5® 30 m x 0.53 mm I.D. with a 1.5 µm film thickness

Temperature program: initial: 170°C, hold 0 min, ramp to 250°C @ 10°C/min; hold 0 min. Retention time : phorate oxon sulfone = 4.87 min. ; phorate sulfone = 5.63 min.  
Both phorate sulfone and phorate oxon sulfone are analyzed during the same

chromatographic run.

**Flows:**

Carrier (He) = 20 mL/min

Make-up (He) = 10 mL/min

Air = 115 mL/min

Hydrogen = 100 mL/min

**B. Auxiliary Apparatus**

1. Rotary platform shaker.
2. 100 mL round bottom flasks.
3. 50 mL graduated cylinders.
4. Rotary evaporator.
5. Disposable pipettes.
6. Separatory funnels, 125 mL.
7. Nitrogen evaporator (N-Evap®).
8. Graduated 15 mL centrifuge tubes.
9. Autosampler vials and screw caps.

**C. Reagents**

1. Ethyl acetate, pesticide grade.
2. Chloroform, pesticide grade.
3. Acetone, pesticide grade.
4. Phorate, American Cyanamid, 97.6 % or equivalent.
5. Phorate sulfone, American Cyanamid 99.0 % or equivalent
6. Phorate oxon sulfone, American Cyanamid 96.0 % or equivalent
7. 20% Magnesium sulfate.
8. 0.5 N Potassium permanganate.
9. Sodium sulfate, anhydrous.
10. Filter paper, Whatman 541, 55 mm circles.

**5. ANALYSIS OF SAMPLES**

1. A solvent blank and/or a control resin blank will be analyzed with each set of samples. The blank must be free of interferences for the analysis of both phorate sulfone and phorate oxon sulfone.
2. Three resin fortification samples must be fortified, extracted and analyzed with each set of samples.
3. Allow samples to come to room temperature and add 75 mL of ethyl acetate.

Cap the sample and swirl for one hour on a rotary platform shaker.

4. Quantitatively transfer 37.5 mL to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator. Add 2 mL of acetone.
5. Add 5 mL of 20% magnesium sulfate solution and swirl. Add 20 mL of 0.5N potassium permanganate solution and swirl. Allow sample to sit for 30 minutes with occasional swirling. Transfer the oxidized mixture to a 125 mL separatory funnel. Rinse the oxidation flask with 20 mL of chloroform and add to the separatory funnel. Shake the funnel for 30 seconds to extract & allow the phases to separate. Drain the lower layer (chloroform) through No. 541 filter paper containing a teaspoonful of granular, anhydrous sodium sulfate into a 250 mL boiling flask. Repeat the extraction twice more with 20 mL portions of chloroform. Rinse the sodium sulfate with 5 mL of chloroform. Evaporate the combined extracts just to dryness on a rotary vacuum evaporator.
6. Transfer sample using small aliquots of ethyl acetate to a graduated centrifuge tube. Adjust sample to an appropriate volume for injection on to the GC-FPD.
7. Transfer an aliquot of the adjusted sample to an Autosampler vial.
8. Inject 3  $\mu$ L of sample, along with the appropriate standard concentrations for phorate sulfone and phorate oxon sulfone, into the gas chromatograph. If the peak height for either the parent or the oxon, is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.
9. Calculate the mass of phorate sulfone and phorate oxon sulfone, in  $\mu$ g, based on the linear regression curve for TurboChrom and the appropriate dilution factors.

$$\text{Concentration } (\mu\text{g/mL}) \times \text{Dilution Factor (mL)/Sample} = \mu\text{g/sample.}$$

10. Calculate the total phorate in each sample using the following equation:

$$\text{Total Phorate } (\mu\text{g}) = \text{Mass phorate sulfone} \times 0.890 + \text{mass phorate oxon sulfone} \times 0.942$$

## 6. QUALITY ASSURANCE

### A. Instrument Reproducibility

Triplicate injections of two standards at five different concentrations were made to establish the reproducibility of the instrument. The data for phorate sulfone is given in Table 1 while the data for phorate oxon sulfone is in Table 2.

Table 1. Instrument Reproducibility for Phorate Sulfone

Phorate sulfone injected (pg/ $\mu$ L)	Integration Counts	Percent (%)
31	7374 $\pm$ 238	$\pm$ 4.15
62	14282 $\pm$ 384	$\pm$ 1.86
125	27930 $\pm$ 928	$\pm$ 3.32
250	55670 $\pm$ 1057	$\pm$ 2.69
500	117318 $\pm$ 4871	$\pm$ 3.23

Table 2. Instrument Reproducibility for Phorate Oxon Sulfone

Phorate oxon sulfone injected (pg/ $\mu$ L)	Integration Counts	Percent (%)
31	1583 $\pm$ 288	$\pm$ 18.2
62	2383 $\pm$ 428	$\pm$ 18.0
125	4928 $\pm$ 454	$\pm$ 9.20
250	11654 $\pm$ 1348	$\pm$ 11.6
500	34160 $\pm$ 2496	$\pm$ 7.31

## B. Linearity

A five point calibration curve of phorate sulfone and phorate oxon sulfone, with concentrations ranging from 0.031  $\mu$ g/mL to 0.50  $\mu$ g/mL, was injected 3 times during the course of a run that included a total of 72 injections. The run included XAD resin samples and fortified resin samples. The corresponding equations and correlation coefficients are:

For phorate sulfone:

$$Y = 234.8271 * x - 783.252 \quad \text{Corr} = 0.9999$$

For phorate oxon sulfone:

$$Y = 70.250 * x - 2669.44 \quad \text{Corr} = 0.9867$$

### C. Minimum Detection Limit

The minimum detection limit (mdl) is set by the minimum concentration injected (31.2 pg/ $\mu$ L) times the minimum total volume (2.0 mL) times the dilution factor (one-half of the sample used). The minimum detectable is 0.13  $\mu$ g/sample.

Assuming a total air sampling rate of 15 Lpm for 24 hours, the total air volume processed would be: 21 m<sup>3</sup> and the air concentration = 0.13  $\mu$ g/21 m<sup>3</sup> = 6.0 ng/m<sup>3</sup>

### D. Laboratory Recovery Data and Air Collection Efficiency (air trapping) of Phorate sulfone and Phorate oxon sulfone

Laboratory recovery data for phorate is given in Table 3 while air collection data for phorate is given in Table 4. A second set of air collection data for phorate is given in Table 6.

Table 3. Laboratory Recovery of Phorate from Resin Spikes

Sample	Date Fortified	Fortification ( $\mu$ g)	Recovery ( $\mu$ g)	% Rec	Phorate Average	Stdev.
243MV50R1	3/21/97	50	41.2	82.4	80.8	2.71
244MV50R2	3/21/97	50	41.2	82.4		
245MV50R3	3/21/97	50	38.9	77.7		
221MV25R5	3/18/97	25	17.1	68.3		
223MV25R6	3/18/97	25	18.7	74.6		
216MV25R1	3/16/97	25	21.1	84.5	79.2	7.44
217MV25R2	3/16/97	25	21.4	85.5		
218MV25R3	3/16/97	25	20.7	82.9		

Table 4. Phorate Air Collection Experiments

Sample 50 (µg)	Sample Period	Glass Wool (µg)	Primary (µg)	Trapping Efficiency (%)	Total Mass Recovery (%)
198/199/200-T	11 hours	0.27	24.6	69.2	69.5
201/202/203-T	11 hours	0.15	20.4	58.1	59.3
207/208/209-T	15 hours	0.35	24.7	58.9	59.3
210/211/212-T	15 hours	0.38	24.8	58.2	59.7
213/214/215-T	15 hours	0.34	24.2	57.8	58.2

A: Samplers ran for 11 or 15 hours @ ~ 20 Lpm; Maximum temperature 20 °C

B: No phorate sulfone or phorate oxon sulfone was found in the back up trap

C: "Trapping Efficiency" is = (Primary (µg) x 100)/(amt. spiked (µg) - amt. recovered on Glass wool)/lab recovery.

D: "Total Mass Recovery" is = [(Glass wool (µg) + Primary (µg)) x 100]/amt. spiked (µg).

Table 5. Phorate Air Collection Experiments, Direct Resin Fortification<sup>A</sup>

Sample 50 (µg)	Primary (µg)	Back up (µg)	Trapping Efficiency Uncorrected (%)	Trapping Efficiency Corrected <sup>B</sup> (%)
236-M	38.5	n.d.	77.1	84.7
237-M	37.3	n.d.	74.6	82.0
238-M	38.2	n.d.	76.4	83.9
239-M	41.2	n.d.	72.4	90.5
240-M	37.0	n.d.	74.0	81.3
241-M	37.6	n.d.	75.2	82.7

A: Samplers ran for 24 hours @ ~ 20 Lpm; Maximum temperature 27 °

B: Trapping efficiency corrected for lab recovery (91%).

#### E. Storage Stability

A 30 day freezer storage stability study for phorate and potential metabolites was initiated on March 9, 1997. These samples will be analyzed during the course of the ambient site sample analysis.



#### **F. Phorate Confirmation**

Selected samples will be confirmed with a Mass Selective Detector in selective ion monitoring mode (SIM). Confirmation will include retention time and visual inspection of the selected ions monitored for sulfone compounds. Additional confirmation may include full spectrum scans and spectral library searches and/or comparison of ion ratios with standards and fortified resin samples. Spectral library searches will depend on the degree of background in the samples and the concentration of the compound of interest. Confirmation will be qualitative not quantitative.

APPENDIX II

LABORATORY REPORT

**Method Development, Ambient Site and Application Site Monitoring  
for Phorate in Air Samples Using XAD-4® Resin as a Trapping Medium**

Takayuki Shibamoto

Charles R. Mourer

Gregory L. Hall

Mathew J. Hengel

June 30, 1997

Revised November 15, 1997

**Trace Analytical Laboratory,**  
Department of Environmental Toxicology,  
University of California, Davis

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Protection Agency

## Disclaimer

The statements and conclusions in the report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

## **Standard Operating Procedure for the Analysis of Phorate in Ambient Air**

### **1. SCOPE**

The method utilized is a gas chromatographic method with a flame photometric detector (FPD) and a 526 nm filter that is selective for phosphorus compounds. This method has been used by Environmental Toxicology personnel for the analysis of organophosphates in air.

### **2. SUMMARY OF METHOD**

Exposed XAD-4<sup>®</sup> resin samples are stored either in an ice chest with dry ice or at -20 °C in a freezer. Samples are extracted with 75 mL of ethyl acetate and an aliquot is oxidized with potassium permanganate to phorate sulfone and phorate oxon sulfone, then concentrated prior to injecting 4 µL on to a gas chromatograph equipped with a flame photometric detector. Results of both compounds are mathematically converted back to parent compound and reported as total phorate.

### **3. INTERFERENCES/LIMITATIONS**

Potential interferences may arise due to contaminants in laboratory solvents, reagents, glassware and/or apparatus. A reagent blank and/or control resin blank must be run through the method procedure and analyzed with each set of samples. We reserve the right to change this standard operating procedure should the need arise to handle unforeseen complications with the compounds of interest.

### **4. EQUIPMENT AND CONDITIONS**

#### **A. Instrumentation**

Hewlett-Packard 5890 Series II gas chromatograph  
Hewlett-Packard 7673 Autosampler  
Perkin-Elmer TurboChrom<sup>®</sup> Data System v. 4.1  
Microsoft Excel<sup>®</sup>, version 7.0

Injector : 250°C

Detector: 225°C

Column: Restek XTI-5<sup>®</sup> 30 m x 0.53 mm I.D. with a 1.5 µm film thickness

Temperature program: initial: 170°C, hold 0 min, ramp to 250°C @ 10°C/min; hold 0 min. Retention time : phorate oxon sulfone = 4.87 min. ; phorate sulfone = 5.63 min. Both phorate sulfone and phorate oxon sulfone are analyzed during the same chromatographic run.

Flows:

Carrier (He) = 20 mL/min

Make-up (He) = 10 mL/min

Air = 115 mL/min

Hydrogen = 100 mL/min

**B. Auxiliary Apparatus**

1. Rotary platform shaker.
2. 100 mL round bottom flasks.
3. 50 mL graduated cylinders.
4. Rotary evaporator.
5. Disposable pipettes.
6. Separatory funnels, 125 mL.
7. Nitrogen evaporator (N-Evap<sup>®</sup>).
8. Graduated 15 mL centrifuge tubes.
9. Autosampler vials and screw caps.

**C. Reagents**

1. Ethyl acetate, pesticide grade.
2. Chloroform, pesticide grade.
3. Acetone, pesticide grade.
4. Phorate, American Cyanamid, 97.6 % or equivalent.
5. Phorate sulfone, American Cyanamid, 99.0 % or equivalent.
6. Phorate sulfoxide, American Cyanamid, 99.0% or equivalent.
7. Phorate oxon, American Cyanamid, 96.0% or equivalent.
8. Phorate oxon sulfone, American Cyanamid, 96.0 % or equivalent.
9. Phorate oxon sulfoxide, American Cyanamid, 92.0% or equivalent.
10. 20% Magnesium sulfate.
11. 0.5 N Potassium permanganate.
12. Sodium sulfate, anhydrous.
13. Filter paper, Whatman 541, 55 mm circles.

## 5. ANALYSIS OF SAMPLES

1. A solvent blank and/or a control resin blank will be analyzed with each set of samples. The blank must be free of interferences for the analysis of both phorate sulfone and phorate oxon sulfone.
2. Three resin fortification samples must be fortified, extracted and analyzed with each set of samples.
3. Allow samples to come to room temperature and add 75 mL of ethyl acetate. Cap the sample and swirl for one hour on a rotary platform shaker.
4. Quantitatively transfer 37.5 mL to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator. Add 2 mL of acetone.
5. Add 5 mL of 20% magnesium sulfate solution and swirl. Add 20 mL of 0.5N potassium permanganate solution and swirl. Allow sample to sit for 30 minutes with occasional swirling. Transfer the oxidized mixture to a 125 mL separatory funnel. Rinse the oxidation flask with 20 mL of chloroform and add to the separatory funnel. Shake the funnel for 30 seconds to extract & allow the phases to separate. Drain the lower layer (chloroform) through No. 541 filter paper containing a teaspoonful of granular, anhydrous sodium sulfate into a 250 mL boiling flask. Repeat the extraction twice more with 20 mL portions of chloroform. Rinse the sodium sulfate with 5 mL of chloroform. Evaporate the combined extracts just to dryness on a rotary vacuum evaporator.
6. Transfer sample using small aliquots of ethyl acetate to a graduated centrifuge tube. Adjust sample to an appropriate volume for injection on to the GC-FPD.
7. Transfer an aliquot of the adjusted sample to an Autosampler vial.
8. Inject 4  $\mu$ L of sample, along with the appropriate standard concentrations for phorate sulfone and phorate oxon sulfone, into the gas chromatograph. If the peak height for either the phorate sulfone or the oxon sulfone, is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.

9. Calculate the mass of phorate sulfone and phorate oxon sulfone, in  $\mu\text{g}$ , based on the linear regression curve for TurboChrom and the appropriate dilution factors.

$$\text{Concentration } (\mu\text{g/mL}) \times \text{Dilution Factor (mL)/Sample} = \mu\text{g/sample.}$$

10. Calculate the total phorate in each sample using the following equation (molar conversion of phorate sulfone and phorate oxon sulfone to parent phorate):

$$\text{Total Phorate } (\mu\text{g}) = \text{Mass phorate sulfone} \times 0.890 + \text{mass phorate oxon sulfone} \times 0.942$$

## 6. QUALITY ASSURANCE

### A. Instrument Reproducibility

Triplicate injections of two standards at five different concentrations were made to establish the reproducibility of the instrument. The data for phorate sulfone is given in Table 1 while the data for phorate oxon sulfone is in Table 2.

Table 1. Instrument Reproducibility for Phorate Sulfone

Phorate sulfone injected (pg/ $\mu\text{L}$ )	Integration Counts	Percent (%)
50	7374 $\pm$ 238	$\pm$ 4.15
100	14282 $\pm$ 384	$\pm$ 1.86
200	27930 $\pm$ 928	$\pm$ 3.32
400	55670 $\pm$ 1057	$\pm$ 2.69
800	117318 $\pm$ 4871	$\pm$ 3.23



Table 2. Instrument Reproducibility for Phorate Oxon Sulfone

Phorate oxon sulfone injected (pg/ $\mu$ L)	Integration Counts	Percent (%)
50	1583 $\pm$ 288	$\pm$ 18.2
100	2383 $\pm$ 428	$\pm$ 18.0
200	4928 $\pm$ 454	$\pm$ 9.20
400	11654 $\pm$ 1348	$\pm$ 11.6
800	34160 $\pm$ 2496	$\pm$ 7.31

#### B. Linearity

A five point calibration curve of phorate sulfone and phorate oxon-sulfone, with concentrations ranging from 0.05  $\mu$ g/mL to 0.80  $\mu$ g/mL, was injected 3 times during the course of a run that included a total of 72 injections. The run included XAD resin samples and fortified resin samples. The corresponding equations and correlation coefficients are:

For phorate sulfone:

$$Y = 234.8271 * x - 783.252 \quad \text{Corr} = 0.9999$$

For phorate oxon sulfone:

$$Y = 70.250 * x - 2669.44 \quad \text{Corr} = 0.9867$$

#### C. Minimum Detection Limit

The minimum detection limit (mdl) is set by the minimum concentration injected (50 pg/ $\mu$ L) times the minimum total volume (1.0 mL) times the dilution factor (one-half of the sample used). The minimum detectable is 0.10  $\mu$ g/sample.

Assuming a total air sampling rate of 15 Lpm for 24 hours, the total air volume processed would be: 21 m<sup>3</sup> and the air concentration = 0.10  $\mu$ g/21 m<sup>3</sup> = 4.8 ng/m<sup>3</sup>

#### D. Laboratory Recovery Data and Air Collection Efficiency (air trapping) of

### Phorate sulfone and Phorate oxon sulfone

Preliminary laboratory recovery data was generated by fortifying XAD resin directly with either 25 or 50 µg of parent phorate, letting the solvent evaporate and then working the fortified resin through the analytical method Laboratory. Preliminary method development recovery data for phorate is given in Table 3.

Table 3. Method Development, Laboratory Recovery of Phorate from Resin Spikes

Sample	Date Fortified	Fortification (µg)	Recovery (µg)	% Rec	Phorate Average	Stdev.
216MV25R1	3/16/97	25	21.1	85%		
217MV25R2	3/16/97	25	21.4	86%		
218MV25R3	3/16/97	25	20.7	83%		
222MV25R5	3/18/97	25	19.2	77%		
223MV25R6	3/18/97	25	21.0	84%		
243MV50R1	3/21/97	50	45.8	92%		
244MV50R2	3/21/97	50	43.8	88%		
245MV50R3	3/21/97	50	40.7	81%	84%	4%

Air collection recovery data (trapping efficiencies) for XAD resin was generated by fortifying the glass wool portion of a sampling train consisting of the glass wool fortified with 50 µg of phorate, a primary trap of 30 mL of XAD resin, and a backup trap also consisting of 30 mL of XAD resin. The backup trap was added to check for potential breakthrough of phorate from the primary trap to the backup. The data for this air collection study is given in Table 4.

Table 4. Phorate Air Collection Experiments <sup>A,B</sup>

Sample 50 (µg)	Sample Period	Glass Wool (µg)	Primary (µg)	Trapping Efficiency Uncorr.(%)	Trapping <sup>C</sup> Efficiency (%)	Total Mass <sup>D</sup> Recovery (%)
198/199/200-T	11 hours	0.27	24.6	50%	59%	59%
207/208/209-T	15 hours	0.35	24.7	50%	59%	59%
210/211/212-T	15 hours	0.38	24.8	50%	59%	60%
213/214/215-T	15 hours	0.34	24.2	49%	58%	58%

A: Samplers ran for 11 or 15 hours @ ~ 20 Lpm; Maximum temperature 20 °C

B: No phorate sulfone or phorate oxon sulfone was found in the back up trap

C: "Trapping Efficiency" is = (Primary (µg) x 100)/(amt. spiked (µg) - amt. recovered on Glass wool)/lab recovery (84%).

D: "Total Mass Recovery" is = [(Glass wool (µg) + Primary (µg)) x 100]/amt. spiked (µg)/lab recovery (84%).

A second air collection study where phorate was directly applied to the resin in the primary trap. This study was conducted to demonstrate that the resin would hold onto phorate once it was trapped on the resin. The data for this study is given in Table 5.

Table 5. Phorate Air Collection Experiments, Direct Resin Fortification<sup>A</sup>

Sample 50 (µg)	Primary (µg)	Back up (µg)	Trapping Efficiency Uncorrected d (%)	Trapping Efficiency Corrected <sup>B</sup> (%)
236-M	38.5	n.d.	70	85%
237-M	37.3	n.d.	67	82%
238-M	38.2	n.d.	69	84%
239-M	41.2	n.d.	75	91%
240-M	37.0	n.d.	67	81%
241-M	37.6	n.d.	68	83%

A: Samplers ran for 24 hours @ ~ 20 Lpm; Maximum temperature 27 °C

B: Trapping efficiency corrected for concurrent lab recovery (82%).

The results of both of these collection studies indicates that there is no breakthrough of phorate from the primary trap to the backup trap.

### **E. Storage Stability**

A 44 day freezer storage stability study for phorate and potential metabolites (phorate oxon and phorate sulfone oxon) was initiated on March 9, 1997. The results for these samples are given in Table 6. At least three concurrent laboratory validation samples were analyzed with the storage stability samples. The results of the stability samples when corrected for recovery of the concurrent laboratory validations samples indicate that there is no significant breakdown of parent or potential metabolite during storage.

Table 6. Phorate Storage Stability Results.

Summary for Phorate Storage Stability Samples Injected on 4/22/97  
Storage Time (3/9/97-4/22/97) = 44 Days Storage

Phorate Fortification (50ug)

Sample TAL #	Phorate Sulfone (ug)	Phorate (ug)	Total % Rec	Adjusted <sup>1</sup> % Rec	Ave % Rec	Stdev
475C	0.04	0.03	(<0.20)			
476TV50R1	39.38	35.04	70%			
477TV50R2	40.93	36.43	73%			
478TV50R3	41.30	36.76	74%		72%	2%
155TS50R1	39.93	35.54	71%	99%		
156TS50R2	39.79	35.41	71%	98%		
157TS50R3	40.70	36.22	72%	100%		
158TS50R4	39.10	34.80	70%	96%	-	
159TS50R5	40.39	35.95	72%	100%	99%	2%

Phorate Sulfoxide Fortification (50ug)

Sample TAL #	Phorate Sulfone (ug)	Phorate Sulfoxide (ug)	Total % Rec	Adjusted <sup>1</sup> % Rec	Ave % Rec	Stdev
161TXS50R1	38.63	36.51	73%	101%		
162TXS50R2	38.02	35.93	72%	100%		
163TXS50R3	37.96	35.87	72%	99%		
164TXS50R4	39.05	36.90	74%	102%		
165TXS50R5	38.33	36.22	72%	100%	101%	1%

Phorate Sulfone Fortification (50ug)

Sample TAL #	Phorate Sulfone (ug)	Total % Rec	Ave % Rec	Stdev
167TNS50R1	37.14	74%		
168TNS50R2	38.99	78%		
169TNS50R3	39.57	79%		
170TNS50R4	38.74	77%		
171TNS50R5	39.80	80%	78%	2%

Adjusted Phorate (ug)= Mass of Phorate Sulfone x 0.890 (molar conversion)

Adjusted Phorate Sulfoxide (ug)= Mass of Phorate Sulfone x 0.945 (molar conversion)

1: Adjusted percent recovery = the total recovery corrected for the concurrent laboratory recovery.

## **F. Phorate Confirmation**

Selected samples will be confirmed with a Mass Selective Detector in selective ion monitoring mode (SIM). Confirmation will include retention time and visual inspection of the selected ions monitored for sulfone compounds. Additional confirmation may include full spectrum scans and spectral library searches and/or comparison of ion ratios with standards and fortified resin samples. Spectral library searches will depend on the degree of background in the samples and the concentration of the compound of interest. Confirmation will be qualitative not quantitative.

### **Instrumentation**

Hewlett-Packard 6890 Gas Chromatograph with integrated autosampler  
Hewlett-Packard 5972 Mass Selective Detector (MSD)  
Hewlett-Packard Chemstation Software, version A.02.00

Injector: 250°C, splitless injection

Detector: 280°C

Column: HP-1701 30 m x 0.25 mm I.D. with a 0.25 µm film thickness

Temperature program: initial: 100°C, hold 2 min., ramp to 250°C @ 15°/min., hold 0 min.

Carrier Gas Flow (He) = 1.0 mL/min

Selected Ion Monitoring:  $m/z$  = 199, 215, and 292 (50 ms Dwell Time)

Retention Time for Phorate Sulfone = 13.42 min.

**Figure 1. Method Schematic of Analysis for Phorate**

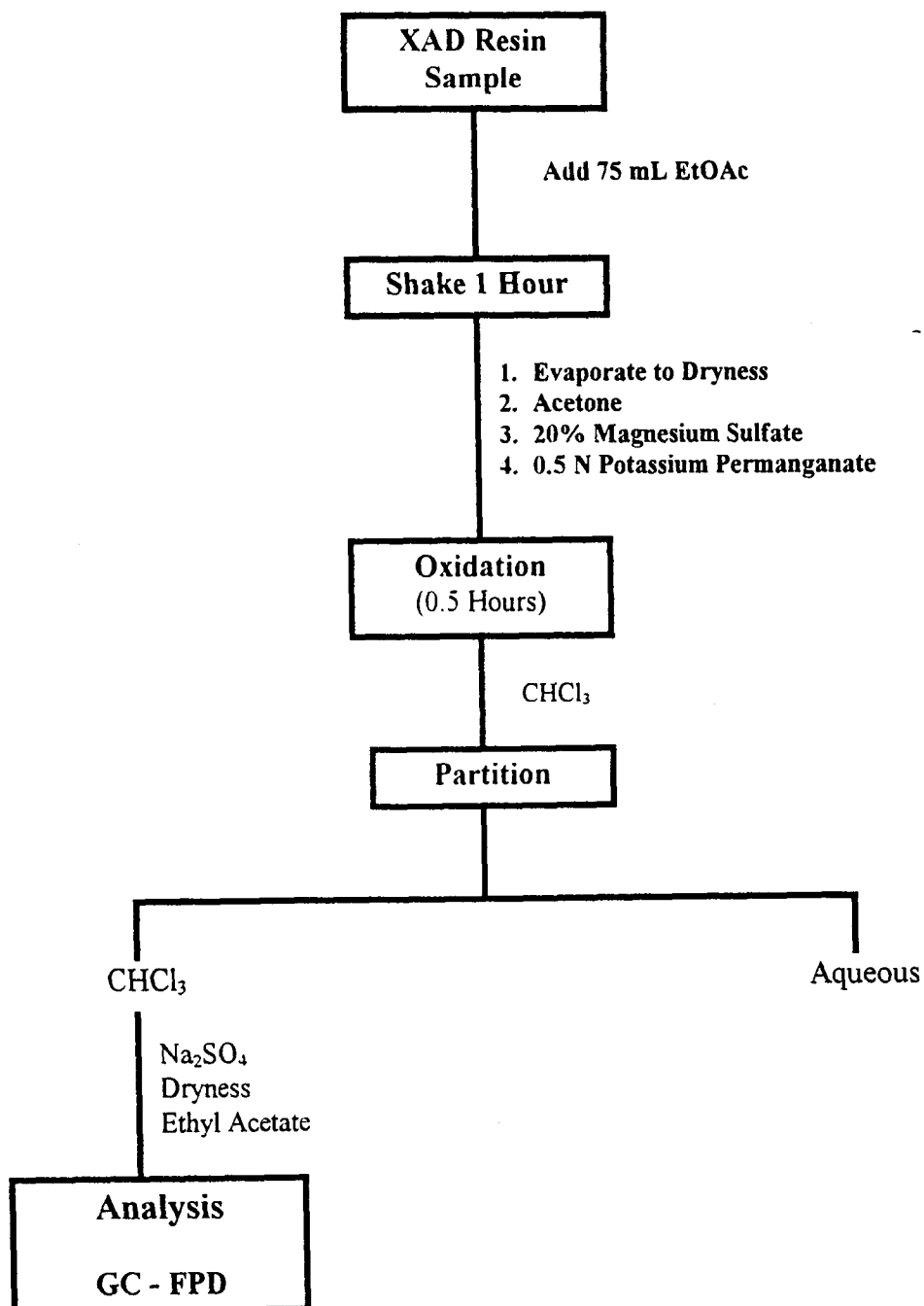


Table 7. Concurrent Laboratory Validation Results (% Recovery)

Sample TAL #	Date Analyzed	Fortification ( $\mu\text{g}$ )	Total Phorate ( $\mu\text{g}$ )	Adjusted % Rec	Ave. % Rec	Stdev
272C	3/28/97	----	<0.20			
273MV0.2R1	3/28/97	0.20	0.19	96%		
274MV0.2R2	3/28/97	0.20	0.21	103%		
275MV0.2R3	3/28/97	0.20	0.20	98%		
302C	4/4/97	----	<0.20			
303MV0.2R4	4/4/97	0.20	0.16	80%		
304MV0.2R5	4/4/97	0.20	0.16	79%		
305MV0.2R6	4/4/97	0.20	0.17	86%		
483C	4/25/97	----	<0.20			
484MV0.2R7	4/25/97	0.20	0.23	113%		
485MV0.2R8	4/25/97	0.20	0.18	92%		
486MV0.2R9	4/25/97	0.20	0.22	110%	95%	12%
353C	4/11/97	----	<0.20			
354MV1.0R1	4/11/97	1.0	0.77	77%		
355MV1.0R2	4/11/97	1.0	0.78	78%		
356MV1.0R3	4/11/97	1.0	0.81	81%		
409C	4/18/97	----	<0.20			
410MV1.0R4	4/18/97	1.0	0.89	89%		
411MV1.0R5	4/18/97	1.0	0.89	89%		
412MV1.0R6	4/18/97	1.0	0.86	86%	83%	5%
539C	5/2/97	----	<0.20			
540MV0.4R1	5/2/97	0.40	0.34	86%		
541MV0.4R2	5/2/97	0.40	0.35	88%		
542MV0.4R3	5/2/97	0.40	0.35	87%	87%	1%
629C	8/29/97	----	<0.20			
630MV50R4	8/29/97	50.0	38.3	77%		
631MV50R5	8/29/97	50.0	39.6	79%		
632MV50R6	8/29/97	50.0	41.0	82%	79%	3%



Table 8. Phorate Ambient Site Results (3/25/97-3/28/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
276	1	SJ-1	<0.20	<0.20	<0.20
277	2	HEL-1	<0.20	<0.20	<0.20
278	3	FP-1	<0.20	<0.20	<0.20
279	4	BOR-1	<0.20	<0.20	<0.20
280	5	ARB-1	<0.20	<0.20	<0.20
281	6	SJ-2	<0.20	<0.20	<0.20
282	7	HEL-2	<0.20	<0.20	<0.20
283	8	FP-2	<0.20	<0.20	<0.20
284	9	BOR-2	<0.20	0.51	0.45*
285	10	ARB-2	<0.20	<0.20	<0.20
286	11	SJ-3	<0.20	<0.20	<0.20
287	12	SJ-3D	<0.20	<0.20	<0.20
288	13	HEL-3	<0.20	<0.20	<0.20
289	14	HEL-3D	<0.20	<0.20	<0.20
290	15	FP-3	<0.20	<0.20	<0.20
291	16	FP-3D	<0.20	<0.20	<0.20
292	17	BOR-3	<0.20	<0.20	<0.20
293	18	BOR-3D	<0.20	<0.20	<0.20
294	19	ARB-3	<0.20	<0.20	<0.20
295	20	ARB-3D	<0.20	<0.20	<0.20
296	21	B-3	<0.20	<0.20	<0.20
297	22	SJ-4	<0.20	<0.20	<0.20
298	23	HEL-4	<0.20	<0.20	<0.20
299	24	FP-4	<0.20	<0.20	<0.20
300	25	BOR-4	<0.20	1.10	0.98*
301	26	ARB-4	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

\*: Analysis by GC/MS could not confirm the presence of Phorate (GC/MS <0.20 µg)

Table 8 Continued. Phorate Ambient Site Results (4/1/97-4/4/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
327	27	SJ-5	<0.20	<0.20	<0.20
328	28	HEL-5	<0.20	<0.20	<0.20
329	29	FP-5	<0.20	<0.20	<0.20
330	30	BOR-5	<0.20	<0.20	<0.20
331	31	ARB-5	<0.20	<0.20	<0.20
332	32	SJ-6	<0.20	<0.20	<0.20
333	33	HEL-6	<0.20	<0.20	<0.20
334	34	FP-6	<0.20	<0.20	<0.20
335	35	BOR-6	<0.20	<0.20	<0.20
336	36	ARB-6	<0.20	<0.20	<0.20
337	37	SJ-7	<0.20	<0.20	<0.20
338	38	SJ-7D	<0.20	<0.20	<0.20
339	39	HEL-7	<0.20	<0.20	<0.20
340	40	HEL-7D	<0.20	<0.20	<0.20
341	41	FP-7	<0.20	<0.20	<0.20
342	42	FP-7D	<0.20	<0.20	<0.20
343	43	BOR-7	<0.20	<0.20	<0.20
344	44	BOR-7D	<0.20	<0.20	<0.20
345	45	ARB-7	<0.20	<0.20	<0.20
346	46	ARB-7D	<0.20	<0.20	<0.20
347	47	Blank	<0.20	<0.20	<0.20
348	48	SJ-8	<0.20	<0.20	<0.20
349	49	HEL-8	<0.20	<0.20	<0.20
350	50	FP-8	<0.20	<0.20	<0.20
351	51	BOR-8	<0.20	<0.20	<0.20
352	52	ARB-8	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

Table 8 Continued. Phorate Ambient Site Results (4/8/97-4/11/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
383	53	SJ-9	<0.20	<0.20	<0.20
384	54	HEL-9	<0.20	<0.20	<0.20
385	55	FP-9	<0.20	<0.20	<0.20
386	56	BOR-9	<0.20	<0.20	<0.20
387	57	ARB-9	<0.20	<0.20	<0.20
388	58	SJ-10	<0.20	<0.20	<0.20
389	59	HEL-10	<0.20	<0.20	<0.20
390	60	FP-10	<0.20	<0.20	<0.20
391	61	BOR-10	<0.20	<0.20	<0.20
392	62	ARB-10	<0.20	<0.20	<0.20
393	63	SJ-11	<0.20	<0.20	<0.20
394	64	SJ-11D	<0.20	<0.20	<0.20
395	65	HEL-11	<0.20	<0.20	<0.20
396	66	HEL-11D	<0.20	<0.20	<0.20
397	67	FP-11	<0.20	<0.20	<0.20
398	68	FP-11D	<0.20	<0.20	<0.20
399	69	BOR-11	<0.20	<0.20	<0.20
400	70	BOR-11D	<0.20	<0.20	<0.20
401	71	ARB-11	<0.20	<0.20	<0.20
402	72	ARB-11D	<0.20	<0.20	<0.20
403	73	SJ-12	<0.20	<0.20	<0.20
404	74	HEL-12	<0.20	<0.20	<0.20
405	75	FP-12	<0.20	<0.20	<0.20
406	76	BOR-12	<0.20	<0.20	<0.20
407	77	ARB-12	<0.20	<0.20	<0.20
408	78	Blank	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

Table 8 Continued. Phorate Ambient Site Results (4/15/97-4/18/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
447	79	SJ-13	<0.20	<0.20	<0.20
448	80	HEL-13	<0.20	<0.20	<0.20
449	81	FP-13	<0.20	<0.20	<0.20
450	82	BOR-13	<0.20	<0.20	<0.20
451	83	ARB-13	<0.20	<0.20	<0.20
453	85	SJ-14	<0.20	<0.20	<0.20
454	86	HEL-14	<0.20	<0.20	<0.20
455	87	FP-14	<0.20	<0.20	<0.20
456	88	BOR-14	<0.20	<0.20	<0.20
457	89	ARB-14	<0.20	<0.20	<0.20
459	91	SJ-15	<0.20	<0.20	<0.20
460	92	SJ-15D	<0.20	<0.20	<0.20
461	93	HEL-15	<0.20	<0.20	<0.20
462	94	HEL-15D	<0.20	<0.20	<0.20
463	95	FP-15	<0.20	<0.20	<0.20
464	96	FP-15D	<0.20	<0.20	<0.20
465	97	B-15	<0.20	<0.20	<0.20
466	98	BOR-15	<0.20	<0.20	<0.20
467	99	BOR-15D	<0.20	<0.20	<0.20
468	100	ARB-15	<0.20	<0.20	<0.20
469	101	ARB-15D	<0.20	<0.20	<0.20
470	102	SJ-16	<0.20	<0.20	<0.20
471	103	HEL-16	<0.20	<0.20	<0.20
472	104	FP-16	<0.20	<0.20	<0.20
473	105	BOR-16	<0.20	<0.20	<0.20
474	106	ARB-16	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

Table 8 Continued. Phorate Ambient Site Results (4/21/97-4/25/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
513	107	SJ-17	<0.20	<0.20	<0.20
514	108	HEL-17	<0.20	<0.20	<0.20
515	109	FP-17	<0.20	<0.20	<0.20
516	110	BOR-17	<0.20	1.05	0.94*
517	111	ARB-17	<0.20	<0.20	<0.20
518	112	SJ-18	<0.20	<0.20	<0.20
519	113	HEL-18	<0.20	<0.20	<0.20
520	114	FP-18	<0.20	<0.20	<0.20
521	115	BOR-18	<0.20	<0.20	<0.20
522	116	ARB-18	<0.20	<0.20	<0.20
523	117	SJ-19	<0.20	<0.20	<0.20
524	118	SJ-19D	<0.20	<0.20	<0.20
525	119	HEL-19	<0.20	<0.20	<0.20
526	120	HEL-19D	<0.20	<0.20	<0.20
527	121	FP-19	<0.20	<0.20	<0.20
528	122	FP-19D	<0.20	<0.20	<0.20
529	123	BOR-19	<0.20	<0.20	<0.20
530	124	BOR-19D	<0.20	<0.20	<0.20
531	125	ARB-19	<0.20	<0.20	<0.20
532	126	ARB-19D	<0.20	<0.20	<0.20
533	127	SJ-20	<0.20	<0.20	<0.20
534	128	HEL-20	<0.20	<0.20	<0.20
535	129	FP-20	<0.20	<0.20	<0.20
536	130	BOR-20	<0.20	<0.20	<0.20
537	131	ARB-20	<0.20	<0.20	<0.20
538	132	Blank	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

\*: Analysis by GC/MS could not confirm the presence of Phorate (GC/MS <0.20 µg)

Table 8 Continued. Phorate Ambient Site Results (4/30/97-5/2/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)
569	133	SJ-21	<0.20	<0.20	<0.20
570	134	HEL-21	<0.20	<0.20	<0.20
571	135	FP-21	<0.20	<0.20	<0.20
572	136	BOR-21	<0.20	<0.20	<0.20
573	137	ARB-21	<0.20	<0.20	<0.20
574	138	SJ-22	<0.20	<0.20	<0.20
575	139	HEL-22	<0.20	<0.20	<0.20
576	140	FP-22	<0.20	<0.20	<0.20
577	141	BOR-22	<0.20	<0.20	<0.20
578	142	ARB-22	<0.20	<0.20	<0.20
579	143	SJ-23	<0.20	<0.20	<0.20
580	144	SJ-23D	<0.20	<0.20	<0.20
581	145	HEL-23	<0.20	<0.20	<0.20
582	146	HEL-23D	<0.20	<0.20	<0.20
583	147	FP-23	<0.20	<0.20	<0.20
584	148	FP-23D	<0.20	<0.20	<0.20
585	149	BOR-23	<0.20	<0.20	<0.20
586	150	BOR-23D	<0.20	<0.20	<0.20
587	151	ARB-23	<0.20	<0.20	<0.20
588	152	ARB-23D	<0.20	<0.20	<0.20
589	153	SJ-24	<0.20	<0.20	<0.20
590	154	HEL-24	<0.20	<0.20	<0.20
591	155	FP-24	<0.20	<0.20	<0.20
592	156	BOR-24	<0.20	<0.20	<0.20
593	157	ARB-24	<0.20	<0.20	<0.20
594	158	Blank	<0.20	<0.20	<0.20

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

Table 9. Trip and Field Spike Results (ARB-QA Ambient)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (ug)	Phorate Sulfone (ug)	Total Phorate (ug)	Average	Stdev
452	84	FS-1	0.15	0.25	0.36		
418	53	FS-2	0.11	0.24	0.32		
458	90	FS-3	0.16	0.23	0.36		
424	59	FS-4	0.14	0.23	0.34		
441	76	FS-5	0.09	0.29	0.34	0.34	0.02
442	77	TS-1	0.05	0.33	0.34		
443	78	TS-2	0.05	0.36	0.37		
444	79	TS-3	0.05	0.36	0.37		
445	80	TS-4	0.04	0.35	0.35		
446	81	TS-5	0.05	0.34	0.35	0.36	0.01

Total Phorate (μg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

Table 10. Application Site Results (8/26/97-8/30/97)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (ug)	Phorate Sulfone (ug)	Total Phorate (ug)
646	14	N1	<0.20	<0.20	<0.20
647	15	W1	<0.20	<0.20	<0.20
648	16	S1	<0.20	<0.20	<0.20
649	17	E1	<0.20	<0.20	<0.20
650	18	E1D	<0.20	<0.20	<0.20
651	19	N2	<0.20	<0.20	<0.20
652	20	W2	<0.20	<0.20	<0.20
653	21	S2	<0.20	<0.20	<0.20
654	22	E2	<0.20	<0.20	<0.20
655	23	E2D	<0.20	<0.20	<0.20
660	24	N3	<0.20	<0.20	<0.20
661	25	W3	<0.20	<0.20	<0.20
662	26	S3	<0.20	<0.20	<0.20
663	27	E3	<0.20	<0.20	<0.20
664	28	E3D	<0.20	<0.20	<0.20
665	29	N4	<0.20	<0.20	<0.20
666	30	W4	<0.20	<0.20	<0.20
667	31	S4	<0.20	<0.20	<0.20
668	32	E4	0.10	0.25	0.32
669	33	E4D	0.11	0.31	0.38
670	34	N5	0.10	0.13	0.21
671	35	W5	<0.20	<0.20	<0.20
672	36	S5	<0.20	<0.20	<0.20
673	37	E5	0.10	0.19	0.27
674	38	E5D	0.11	0.21	0.30
675	39	N6	<0.20	<0.20	<0.20
676	40	W6	0.10	0.27	0.33
677	41	S6	<0.20	<0.20	<0.20
678	42	E6	0.09	0.24	0.30
679	43	E6D	0.10	0.31	0.36
680	44	N7	<0.20	<0.20	<0.20
681	45	W7	0.11	0.38	0.45
682	46	S7	<0.20	<0.20	<0.20
683	47	E7	<0.20	<0.20	<0.20
684	48	E7D	<0.20	<0.20	<0.20

Total Phorate (ug) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)



Table 11. Field, Trip, and Lab Spike Results (ARB-QA Application)

TAL #	ARB Log #	ARB ID	Phorate Oxon Sulfone (µg)	Phorate Sulfone (µg)	Total Phorate (µg)	Average	Stdev
633	1	NB	<0.20	<0.20	<0.20		
634	2	NFS1	<0.20	0.52	0.46		
635	3	WB	<0.20	<0.20	<0.20		
636	4	WFS2	<0.20	0.50	0.45		
637	5	SB	<0.20	<0.20	<0.20		
638	6	SFS3	<0.20	0.48	0.43		
639	7	EB	<0.20	<0.20	<0.20		
640	8	EFS4	<0.20	0.48	0.43	0.44	0.02
641	9	TB	<0.20	<0.20	<0.20		
642	10	TS1	<0.20	0.49	0.43		
643	11	TS2	<0.20	0.47	0.42		
644	12	TS3	<0.20	0.46	0.41		
645	13	TS4	<0.20	0.56	0.50	0.44	0.04
656	A	LS1	<0.20	0.47	0.42		
657	B	LS2	<0.20	0.50	0.45		
658	C	LS3	<0.20	0.45	0.40		
659	D	LS4	<0.20	0.49	0.44	0.43	0.02

Total Phorate (µg) = Mass of phorate sulfone x 0.890 (molar conversion) + mass of phorate oxon sulfone x 0.942 (molar conversion)

**Table 12. Qualitative MSD Confirmation Results**

Sample ID	Sample Type	MSD Analysis Date	Phorate
Standard	50 pg/ $\mu$ L	4/03/97	+
272C	Control Resin	4/03/97	-
274MV0.2R2	0.2 $\mu$ g Resin Fort	4/03/97	+
284 (BOR-2)	Ambient Air Sample	4/03/97	-
285 (ARB-2)	Ambient Air Sample	4/03/97	-
292 (BOR-3)	Ambient Air Sample	4/03/97	-
300 (BOR-4)	Ambient Air Sample	4/03/97	-
Standard	50 pg/ $\mu$ L	4/08/97	+
302C	Control Resin	4/08/97	-
303MV0.2R4	0.2 $\mu$ g Resin Fort	4/08/97	+
332 (SJ-6)	Ambient Air Sample	4/08/97	-
334 (FP-6)	Ambient Air Sample	4/08/97	-
335 (BOR-6)	Ambient Air Sample	4/08/97	-
Standard	50 pg/ $\mu$ L	4/15/97	+
353C	Control Resin	4/15/97	-
354MV1.0R1	1.0 $\mu$ g Resin Fort	4/15/97	+
386 (BOR-9)	Ambient Air Sample	4/15/97	-
387 (ARB-9)	Ambient Air Sample	4/15/97	-
392 (ARB-10)	Ambient Air Sample	4/15/97	-
Standard	50 pg/ $\mu$ L	4/21/97	+
409C	Control Resin	4/21/97	-
412MV1.0R6	1.0 $\mu$ g Resin Fort	4/21/97	+
447 (SJ-13)	Ambient Air Sample	4/21/97	-
450 (BOR-13)	Ambient Air Sample	4/21/97	-
456 (BOR-14)	Ambient Air Sample	4/21/97	-

**Table 12 Cont. Qualitative MSD Confirmation Results**

Standard	50 pg/ $\mu$ L	4/29/97	-
483C	Control Resin Sample	4/29/97	-
484MV0.2R7	0.20 $\mu$ g Fort	4/29/97	+
516 (BOR-17)	Ambient Air Sample	4/29/97	-
521(BOR-18)	Ambient Air Sample	4/29/97	-
531(ARB-19)	Ambient Air Sample	4/29/97	-
539C	Control Resin	5/6/97	-
541MV0.4R2	0.40 $\mu$ g Fort	5/6/97	+
588(ARB-23D)	Ambient Air Sample	5/6/97	-
592(BOR-24)	Ambient Air Sample	5/6/97	-
593(ARB-24)	Ambient Air Sample	5/6/97	-
629C	Control Resin Sample	9/2/97	-
630MV50R4	50 $\mu$ g Resin Fort	9/2/97	+
Standard	50 pg/ $\mu$ L	9/2/97	+
668 (E4)	Application Air Sample	9/2/97	+
669 (E4D)	Application Air Sample	9/2/97	+
670 (N5)	Application Air Sample	9/2/97	+
671 (W5)	Application Air Sample	9/2/97	+

A (+) denotes a positive hit for phorate sulfone equal or greater than 0.10  $\mu$ g/sample, while a (-) denotes a negative hit or residue levels below 0.10  $\mu$ g/sample.

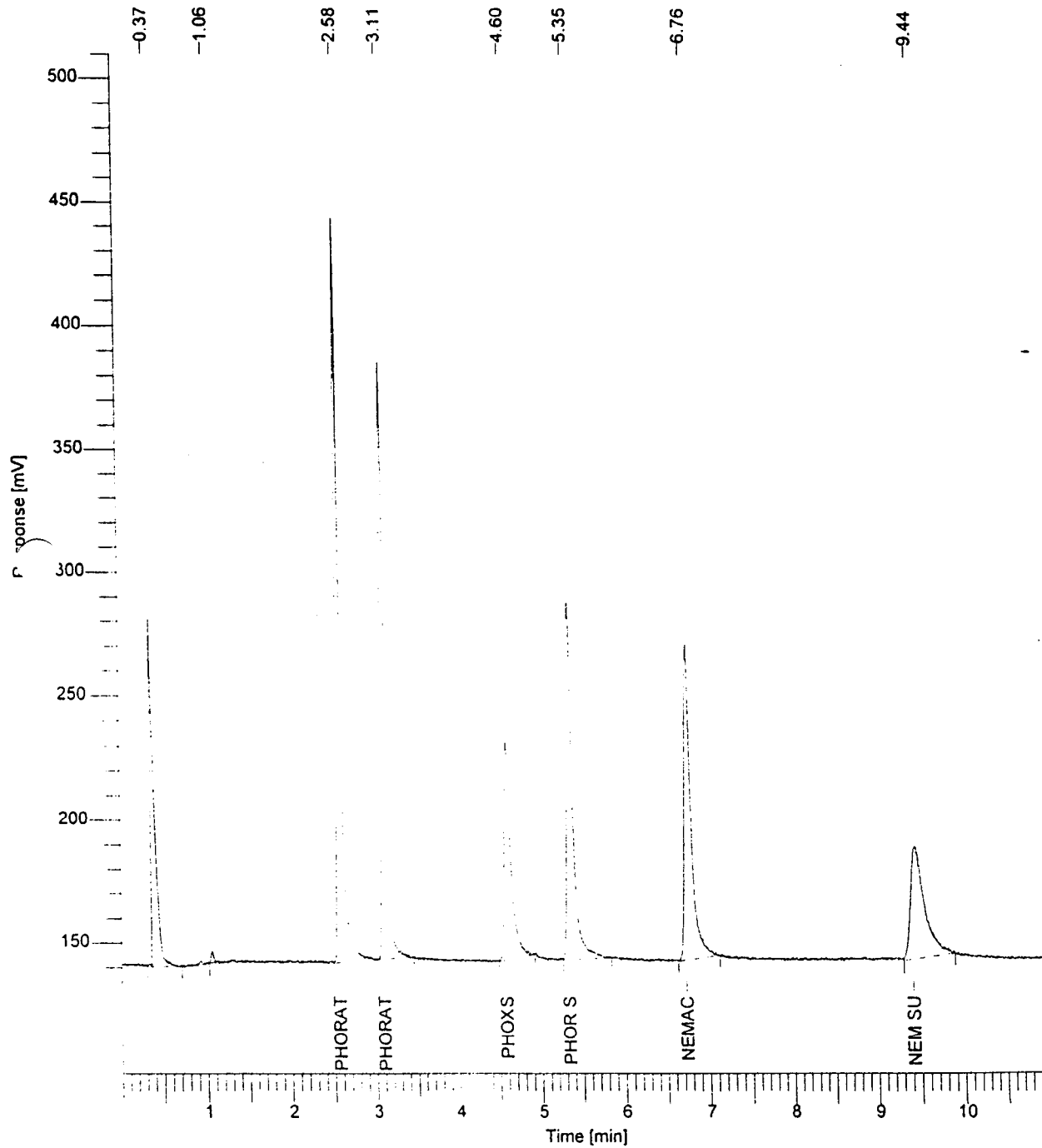
## APPENDIX A. GC and GC/MS Sample Chromatograms.

1. Calibration Standard (GC-FPD), 400 pg/ $\mu$ L Phorate Oxon Sulfone (PHOXS) and Phorate Sulfone (PHOR S).
2. Calibration Standard (GC-FPD), 50 pg/ $\mu$ L Phorate Oxon Sulfone (PHOXS) and Phorate Sulfone (PHOR S).
3. Resin Blank (GC-FPD).
4. Resin Spike, 50  $\mu$ g (GC-FPD).
5. Monitoring Sample (GC-FPD).
6. Application Sample (GC-FPD).
7. ARB-QA Field Spike (GC-FPD).
8. ARB-QA Trip Spike (GC-FPD).
9. ARB-QA Lab Spike (GC-FPD).
10. Storage Stability Sample, 50  $\mu$ g (GC-FPD).
11. Calibration Standard (GC/MS), 50 pg/ $\mu$ L Phorate Sulfone.
12. Resin Blank (GC/MS).
13. Resin Spike, 0.2  $\mu$ g (GC/MS).
14. Monitoring Sample (GC/MS).
15. Monitoring Sample (GC/MS).
16. Application Sample (GC/MS).
17. Application Sample (GC/MS).

# Chromatogram

Sample Name : Std      Sample #: 400pg/ul      Page 1 of 1  
FileName : X:\Data\WPD\_FPD\Arb\_97\Thi\_Nem\082997\829X002-19970830-005844.raw  
Date : 08/31/97 05:37:06 PM  
Method : Nem\_fpd      Time of Injection: 08/30/97 12:58:28 AM  
Stop Time : 0.00 min      End Time : 11.00 min      Low Point : 135.00 mV      High Point : 510.00 mV  
Signal factor: 0.0      Plot Offset: 135.00 mV      Plot Scale: 375.0 mV

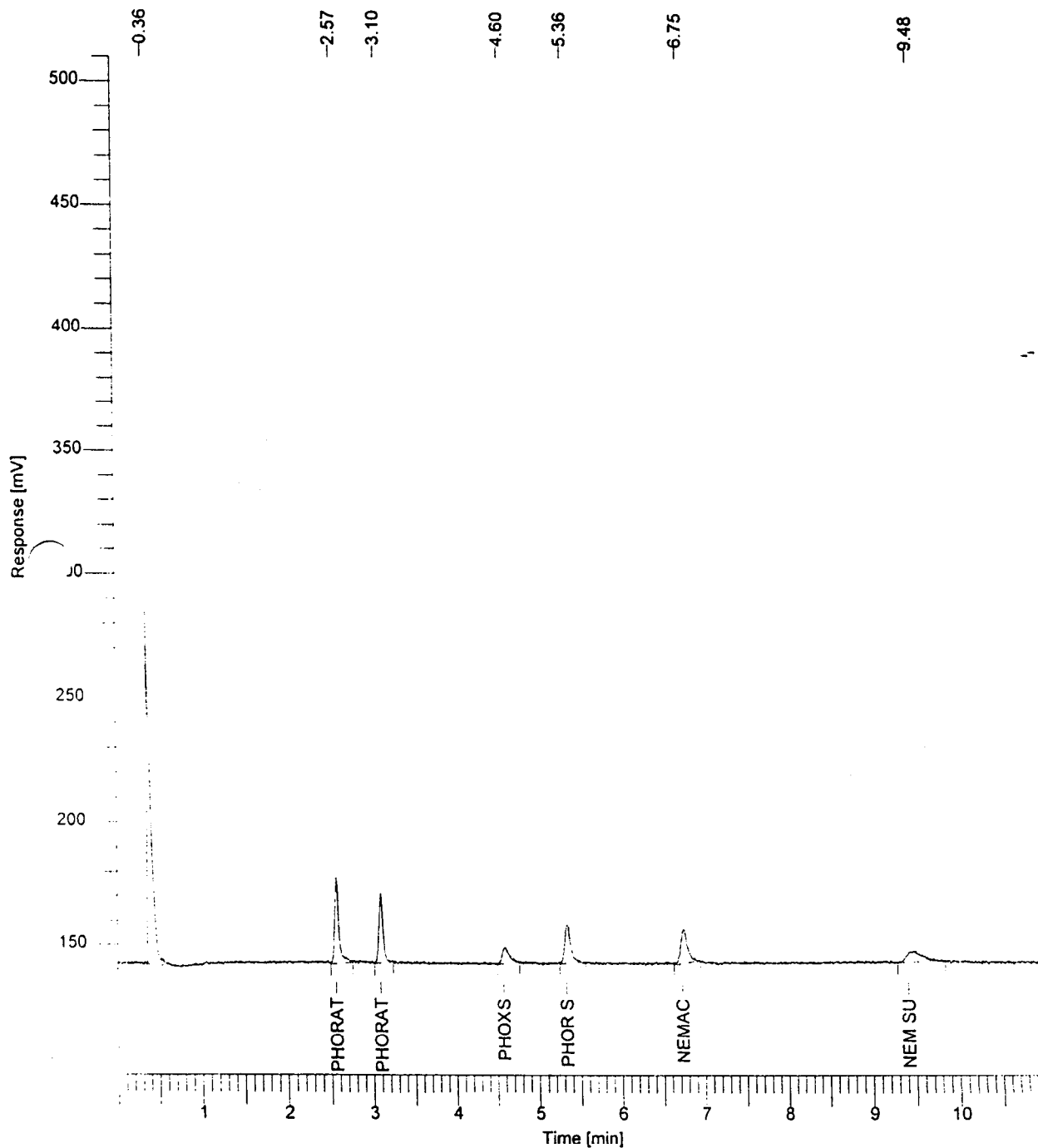
Chromatogram 1



# Chromatogram

Sample Name : Std  
File Name : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X005-19970830-014046.raw  
Date : 08/31/97 05:37:32 PM  
Method : Nem\_fpd  
Start Time : 0.00 min  
End Time : 11.00 min  
Time of Injection : 08/30/97 01:40:28 AM  
Low Point : 135.00 mV  
High Point : 510.00 mV  
Scan Rate : 0.0  
Plot Offset : 135.00 mV  
Plot Scale : 375.0 mV

Chromatogram 2



# Chromatogram

Sample Name : Control

Sample #: 629C

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X006-19970830-015447.raw

Date : 08/31/97 05:37:41 PM

Method : Nem\_fpd

Time of Injection: 08/30/97 01:54:29 AM

Start time : 0.00 min

End Time : 11.00 min

Low Point : 135.00 mV

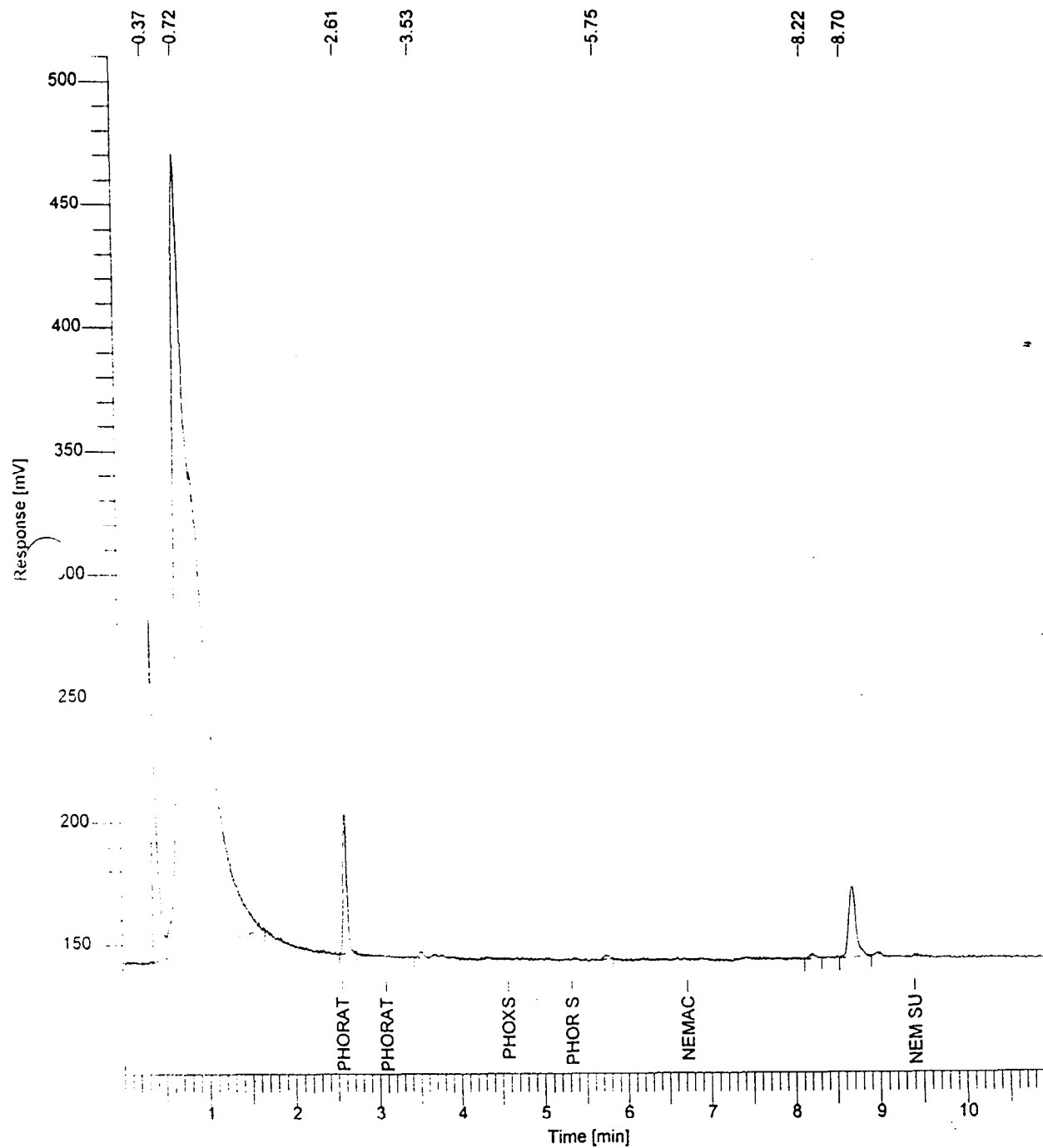
High Point : 510.00 mV

Scan rate: 0.0

Plot Offset: 135.00 mV

Plot Scale: 375.0 mV

## Chromatogram 3



# Chromatogram

Sample Name : Recovery

Sample #: 630MV50R4

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X008.raw

Date : 08/31/97 05:37:58 PM

Method : Nem\_fpd

Time of Injection: 08/30/97 02:22:28 AM

Start Time : 0.00 min

End Time : 11.00 min

Low Point : 135.00 mV

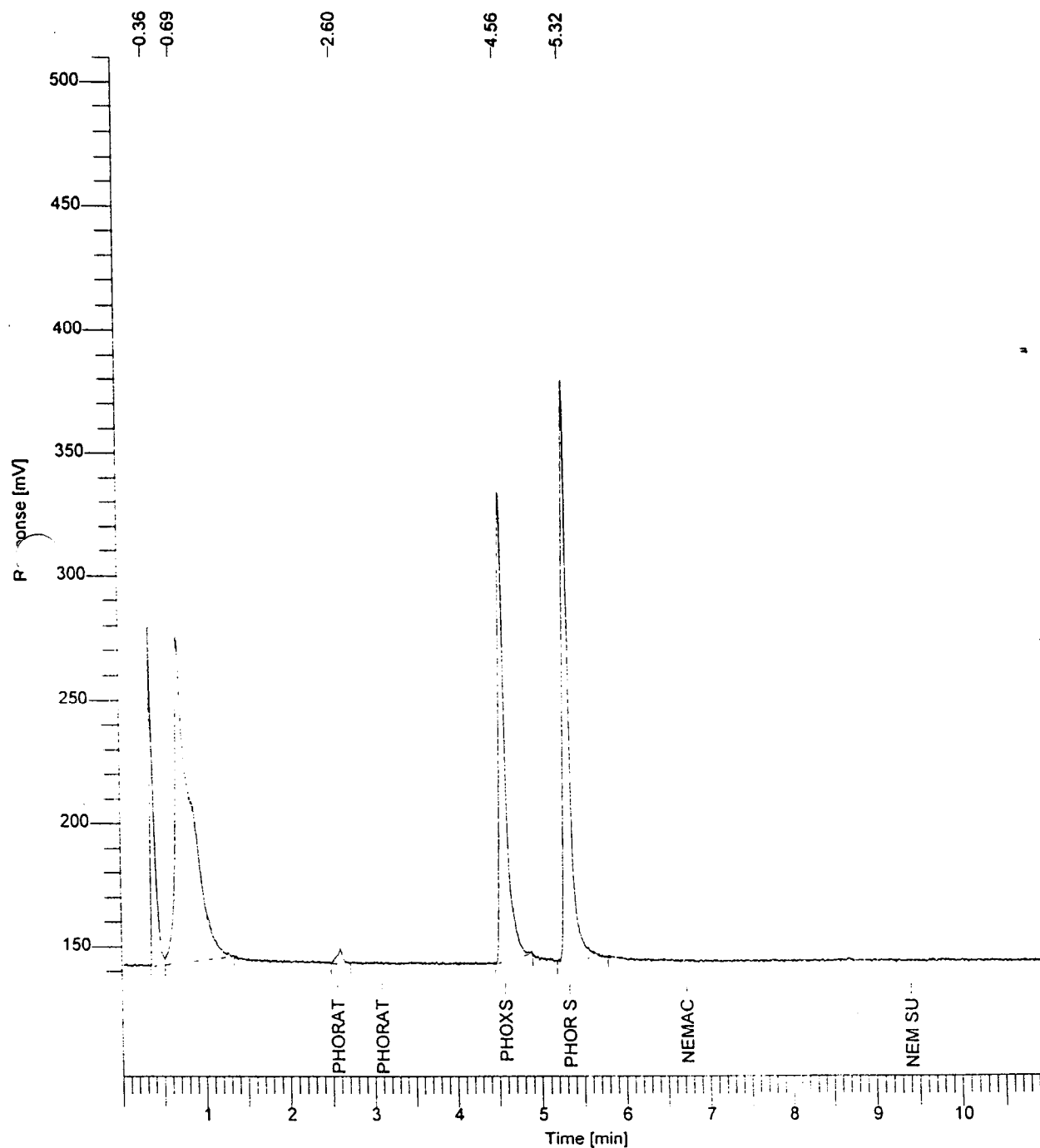
High Point : 510.00 mV

Scale Factor: 0.0

Plot Offset: 135.00 mV

Plot Scale: 375.0 mV

Chromatogram 4





# Chromatogram

Sample Name : HEL-21  
FileName : X:\DATA\NPD\_FPD\ARB\_97\THI\_NEM\050297\502A104  
Method : NEM\_FPD  
Start Time : 0.00 min  
Scale Factor: 0.0

End Time : 11.00 min  
Plot Offset: 135 mV

Sample #: 570

Date : 5/5/97 10:15 AM

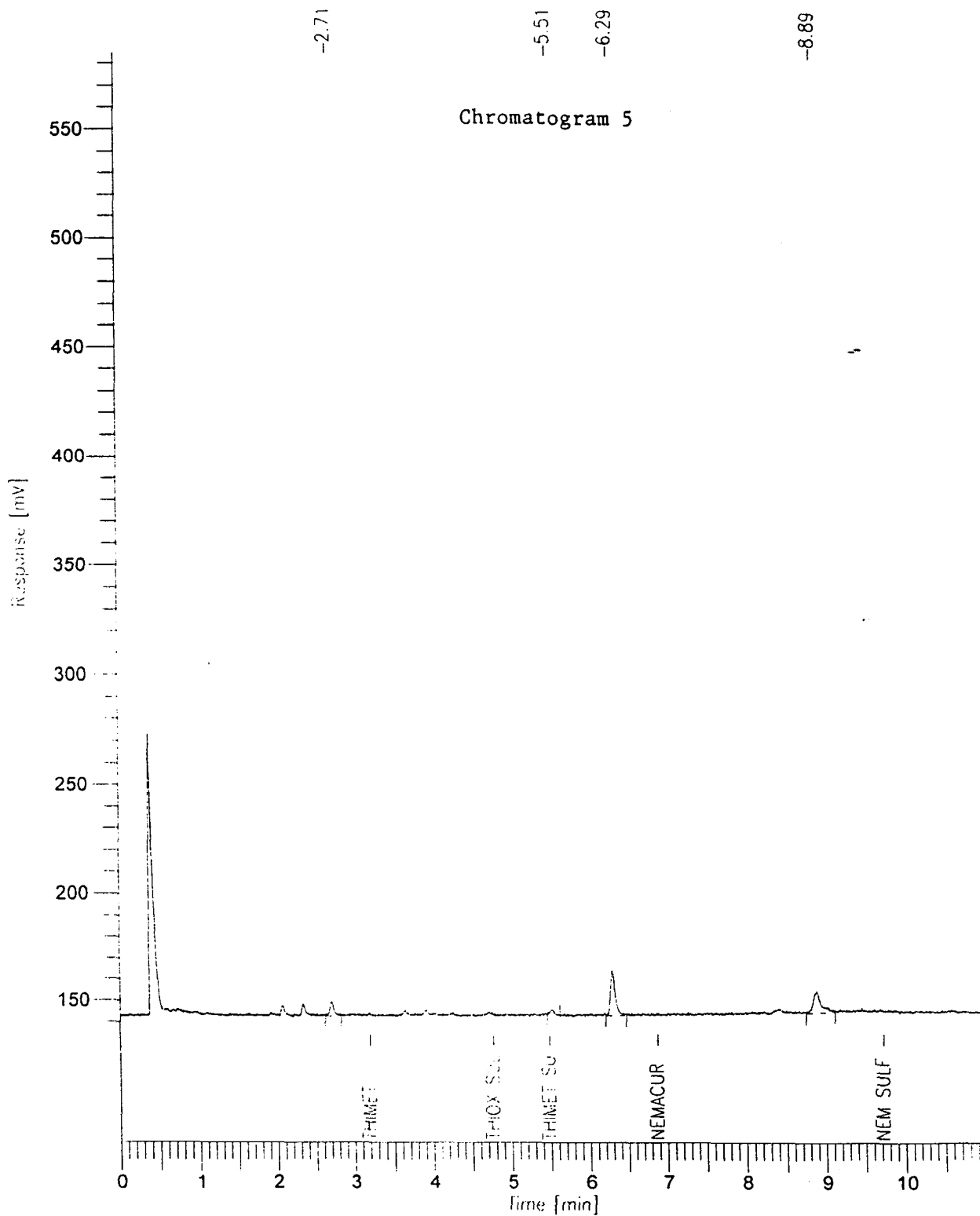
Time of Injection: 5/3/97 04:59 PM

Low Point : 135.00 mV

Plot Scale: 450.0 mV

Page 1 of 1

High Point : 585.00 mV



# Chromatogram

Sample Name : W7

Sample #: 681

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\090197\901A096.raw

Date : 09/04/97 09:43:22 AM

Method : Nem\_fpd

Time of Injection: 09/02/97 03:10:07 PM

Start Time : 0.00 min

End Time : 14.00 min

Low Point : 135.00 mV

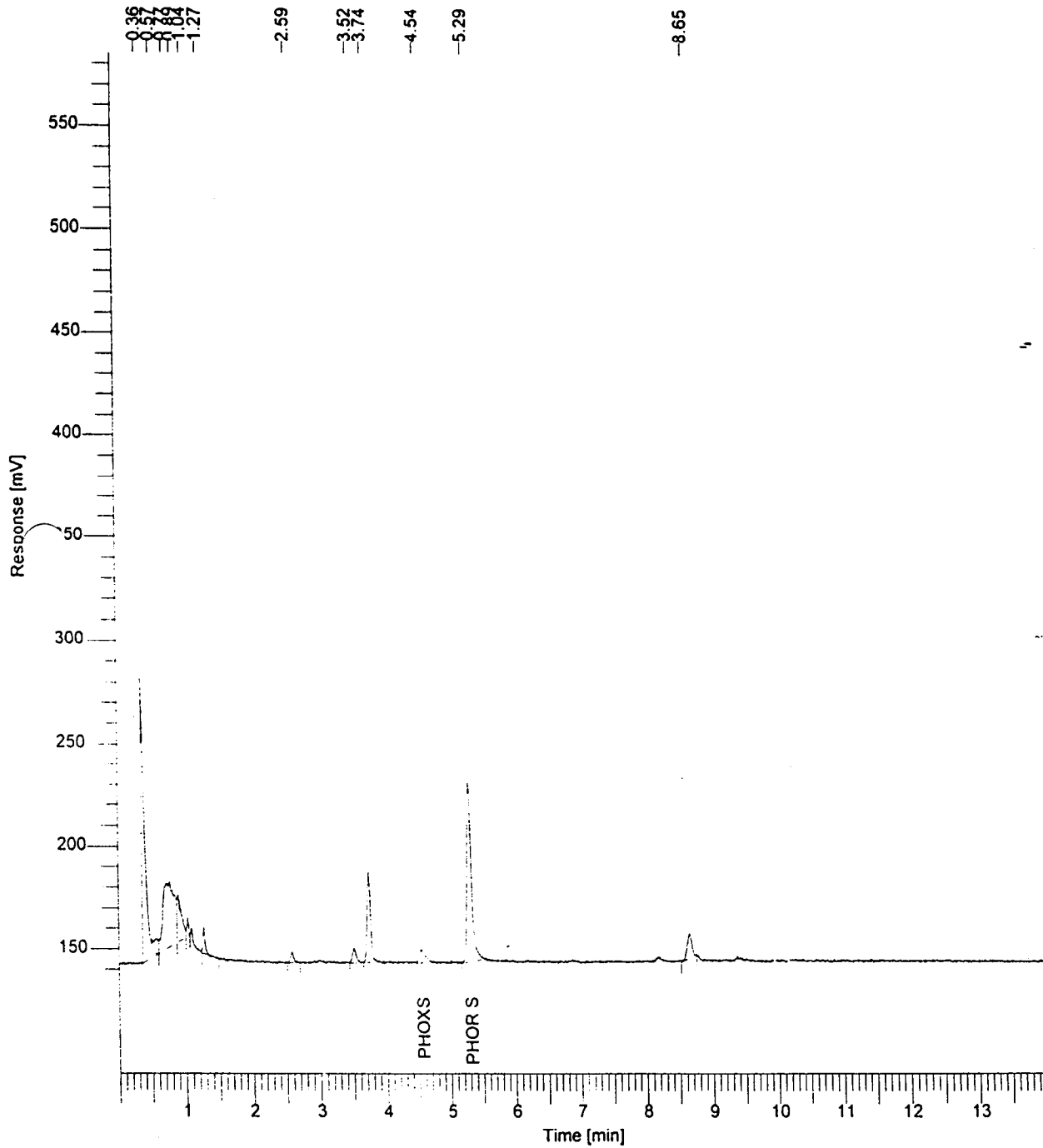
High Point : 585.00 mV

Scale Factor: 0.0

Plot Offset: 135.00 mV

Plot Scale: 450.0 mV

## Chromatogram 6



# Chromatogram

Sample Name : NFS1

Sample #: 634

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X022.raw

Date : 08/31/97 05:39:56 PM

Method : Nem\_fpd

Time of Injection: 08/30/97 05:38:32 AM

Start Time : 0.00 min

End Time : 11.00 min

Low Point : 135.00 mV

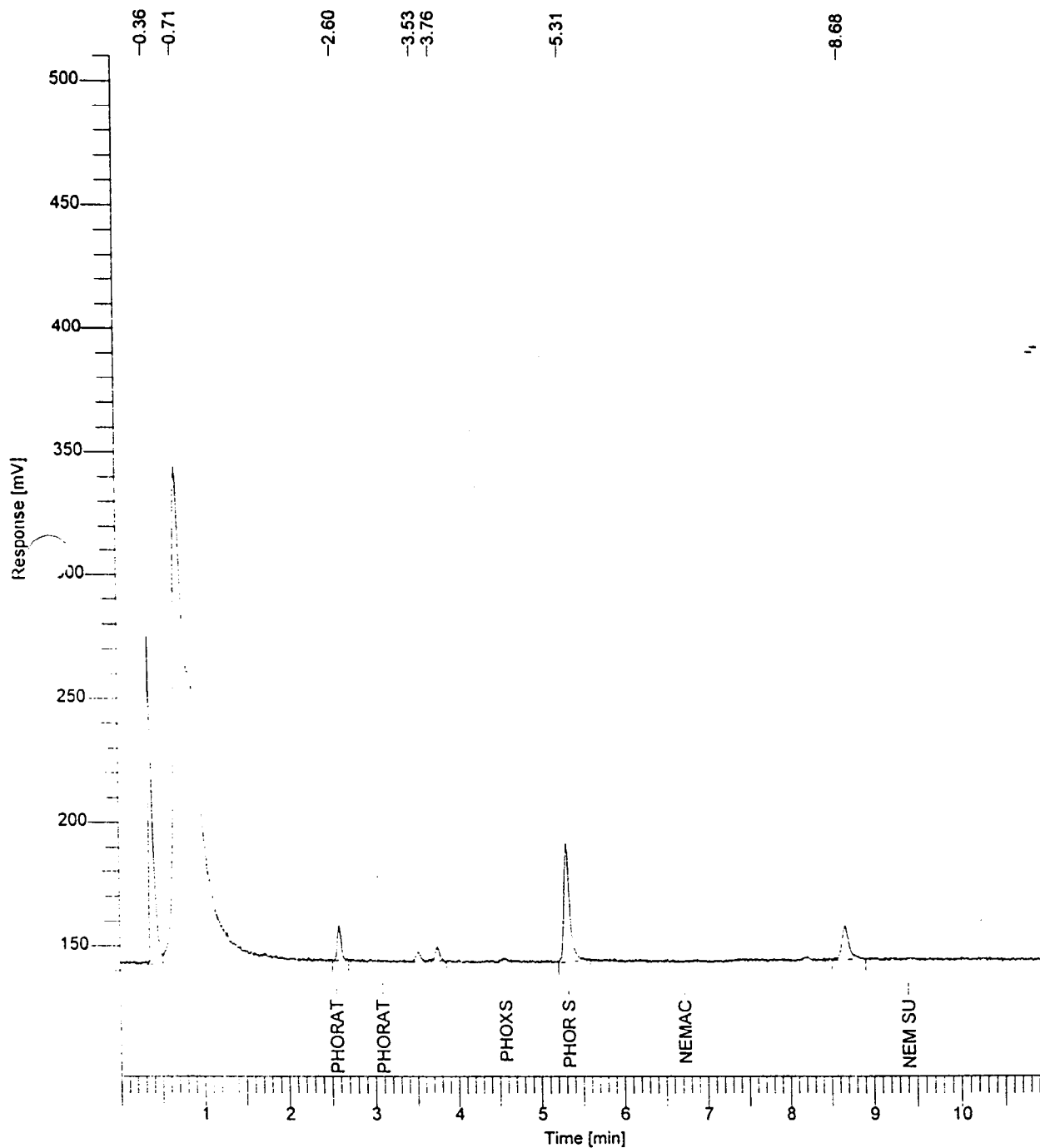
High Point : 510.00 mV

Scale factor: 0.0

Plot Offset: 135.00 mV

Plot Scale: 375.0 mV

## Chromatogram 7



# Chromatogram

Sample Name : TS1

Sample #: 642

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X046.raw

Date : 08/31/97 05:43:12 PM

Method : Nem\_fpd

Time of Injection : 08/30/97 11:14:36 AM

Start Time : 0.00 min

End Time : 11.00 min

Low Point : 135.00 mV

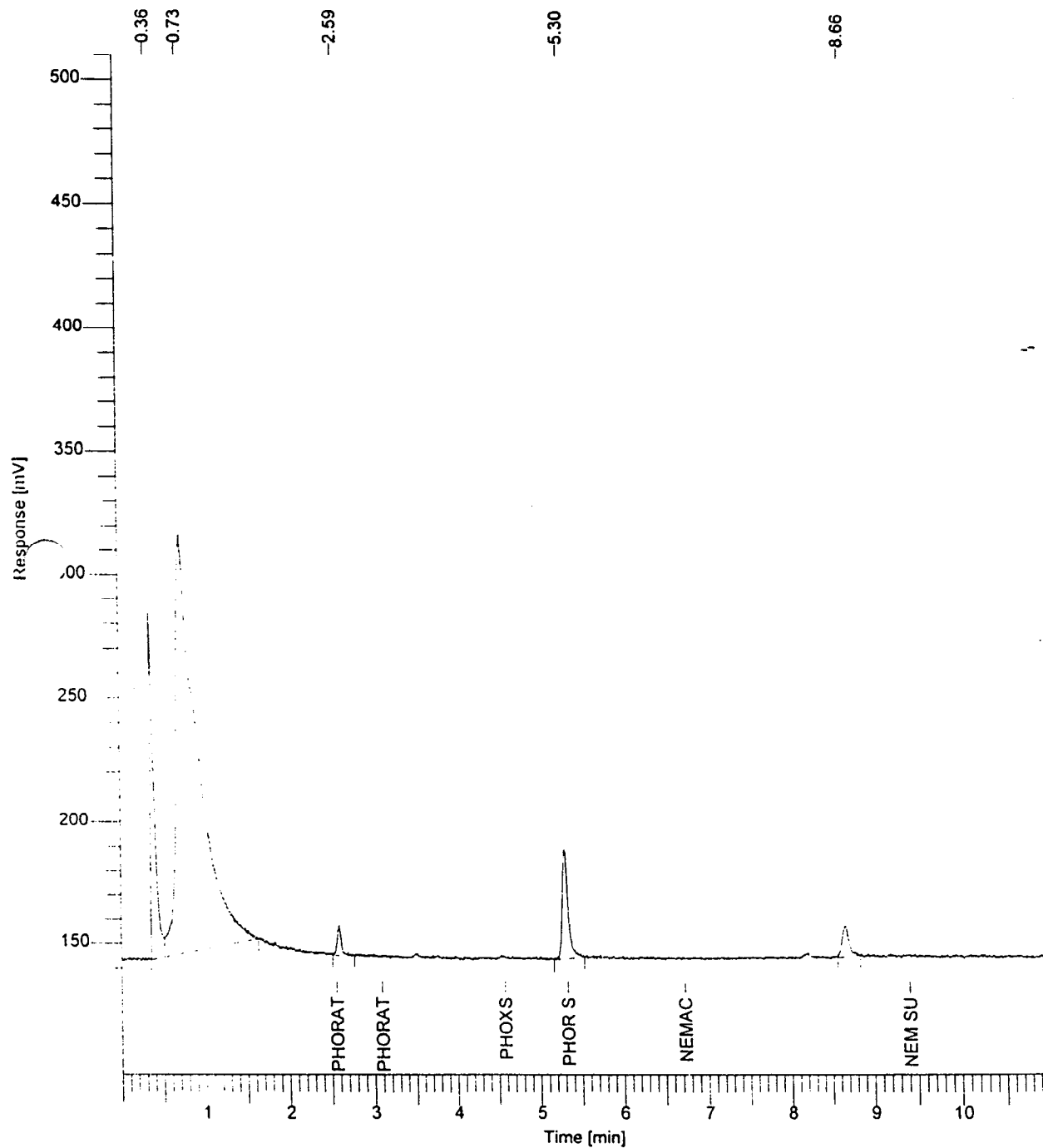
High Point : 510.00 mV

Scactor : 0.0

Plot Offset : 135.00 mV

Plot Scale : 375.0 mV

## Chromatogram 8



# Chromatogram

Sample Name : LS2

Sample #: 857

Page 1 of 1

FileName : X:\Data\NPD\_FPD\Arb\_97\Thi\_Nem\082997\829X059.raw

Date : 08/31/97 05:44:55 PM

Method : Nem\_fpd

Time of Injection: 08/30/97 02:16:50 PM

Stop Time : 0.00 min

End Time : 11.00 min

Low Point : 135.00 mV

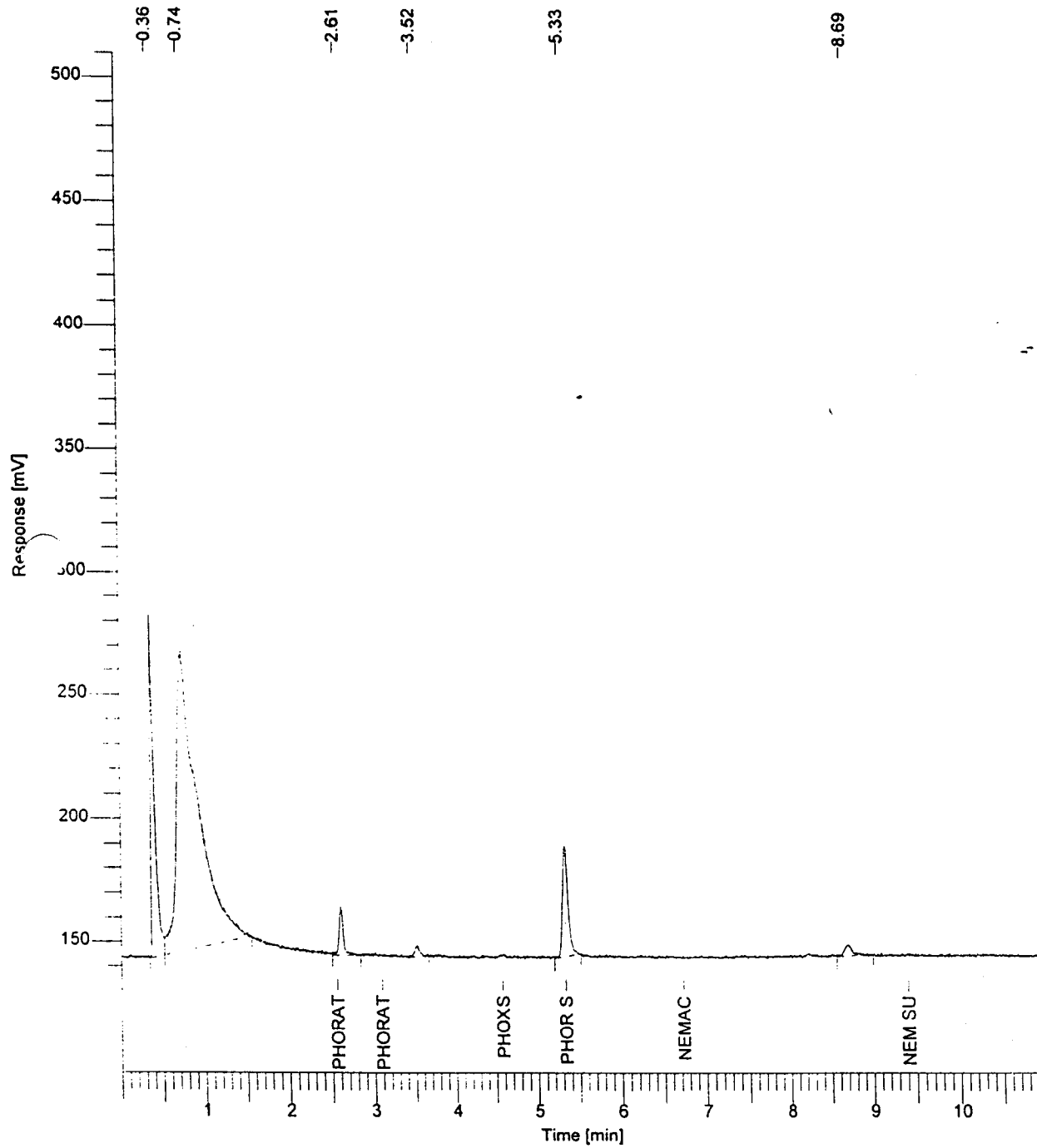
High Point : 510.00 mV

Scan Rate : 0.0

Plot Offset: 135.00 mV

Plot Scale: 375.0 mV

## Chromatogram 9



# Chromatogram

Sample Name : Stability

Sample #: 159TS50R5

Page 1 of 1

FileName : X:\DATA\NPD\_FPD\ARB\_97\THI\_NEM\042297\422A030.raw

Date : 10/08/97 12:16:55 PM

Time of Injection: 04/23/97 12:28:50 AM

Start Time : 0.00 min

End Time : 11.00 min

Low Point : 134.82 mV

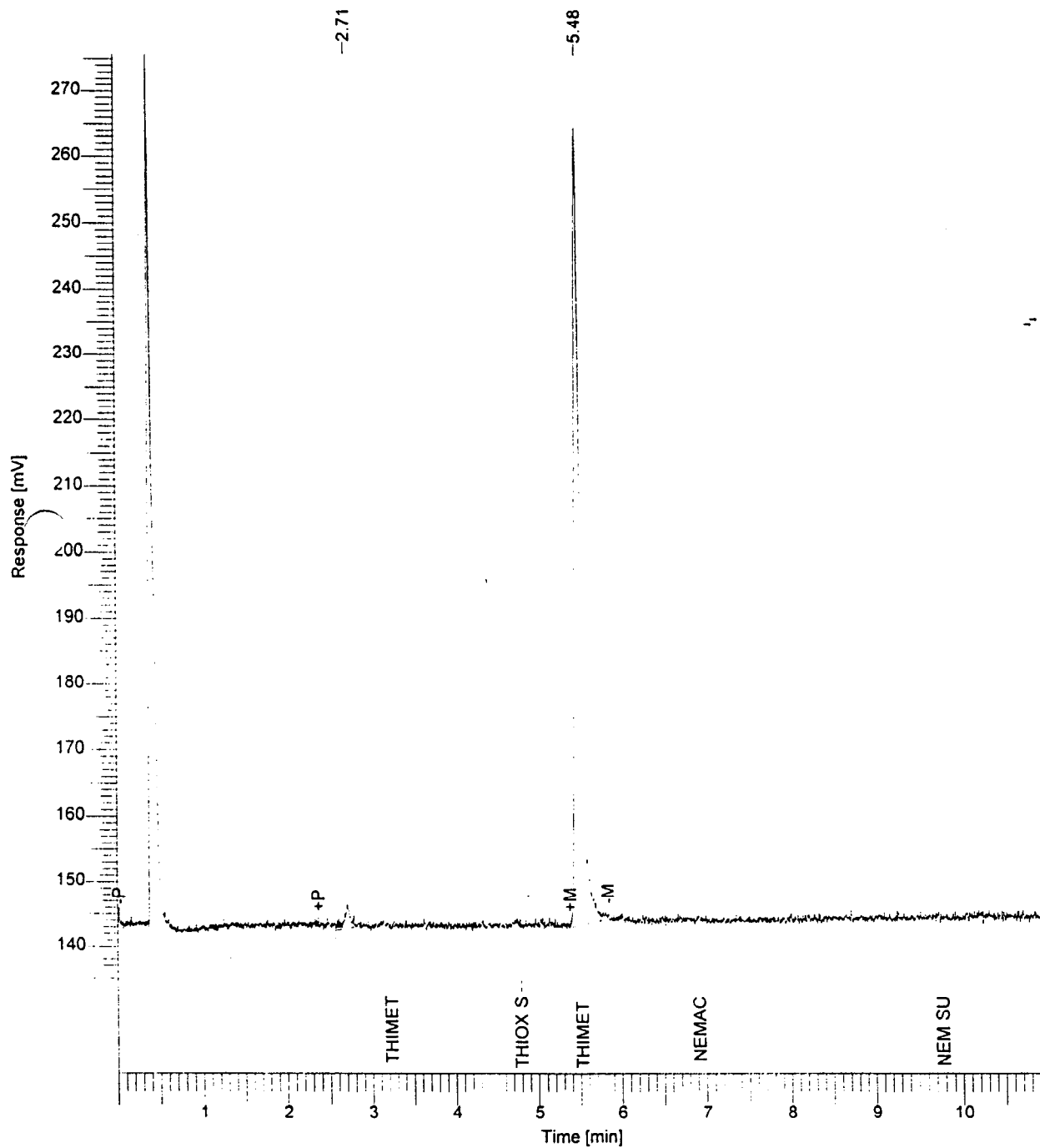
High Point : 275.76 mV

Scale Factor : 0.0

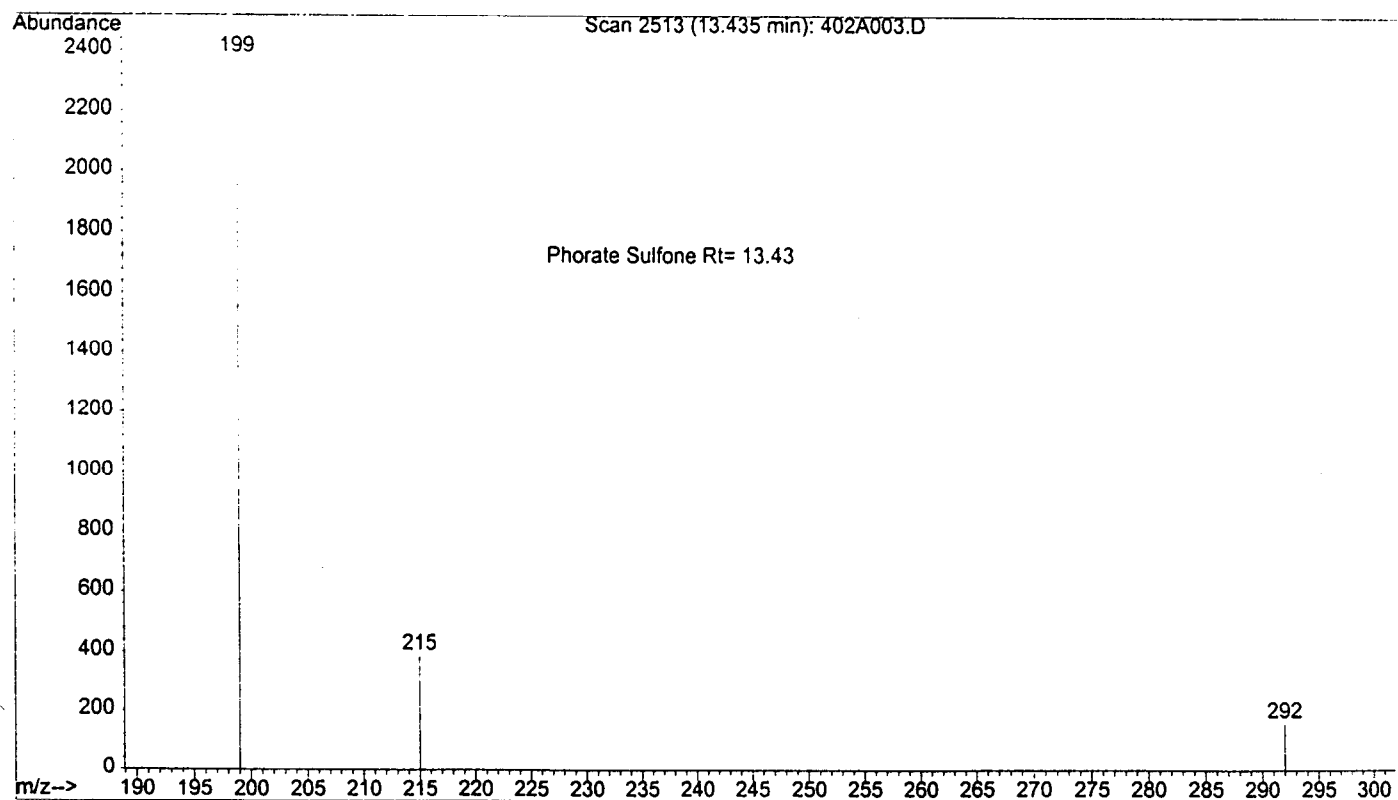
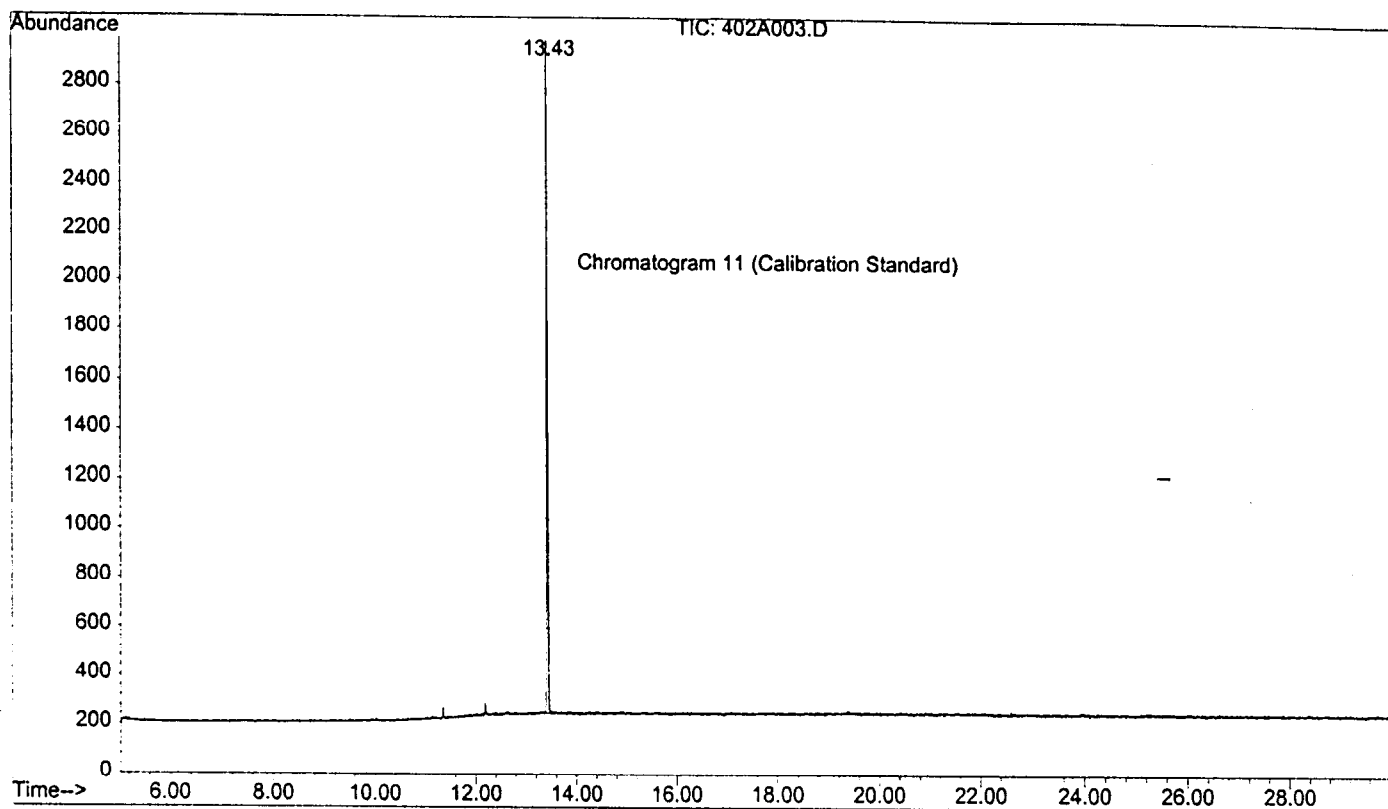
Plot Offset: 134.82 mV

Plot Scale: 140.9 mV

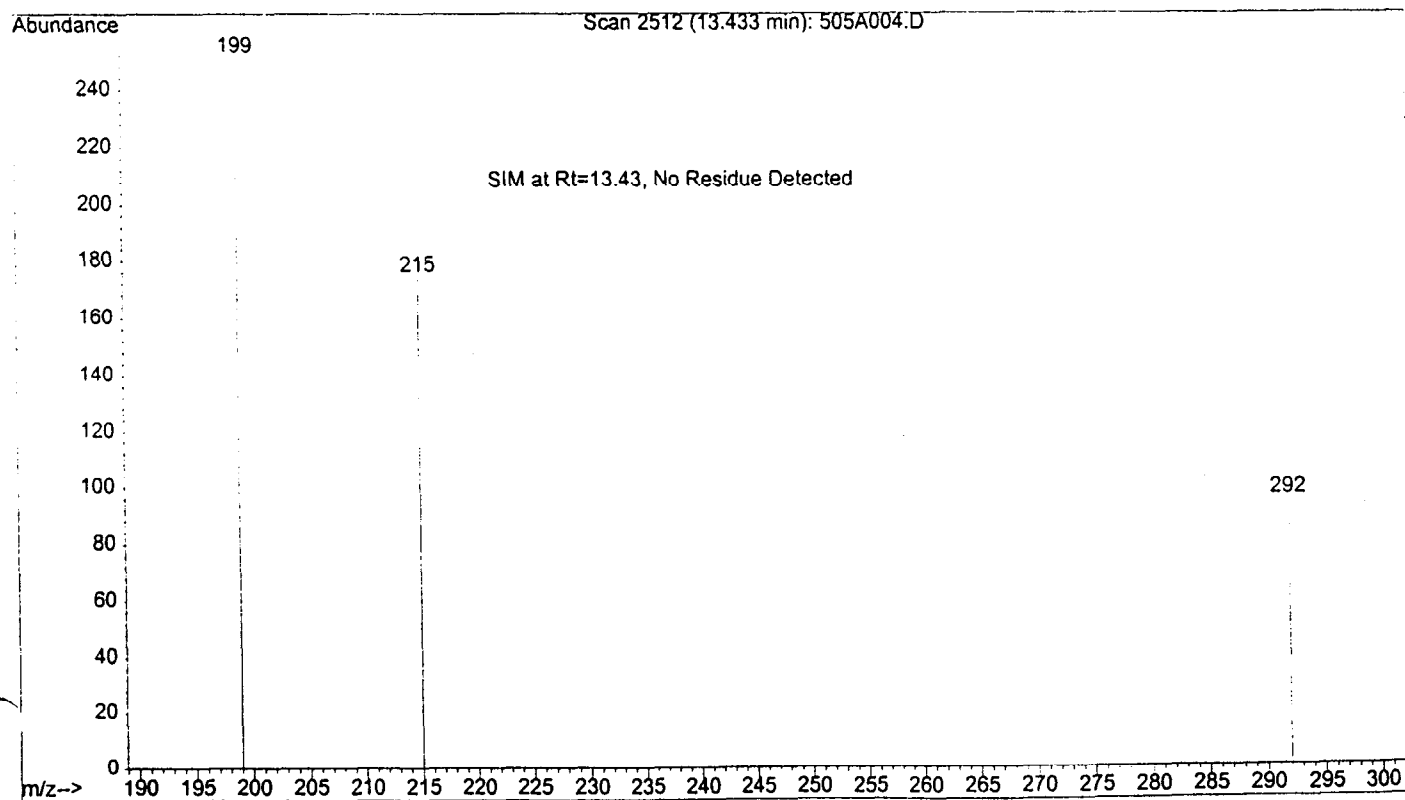
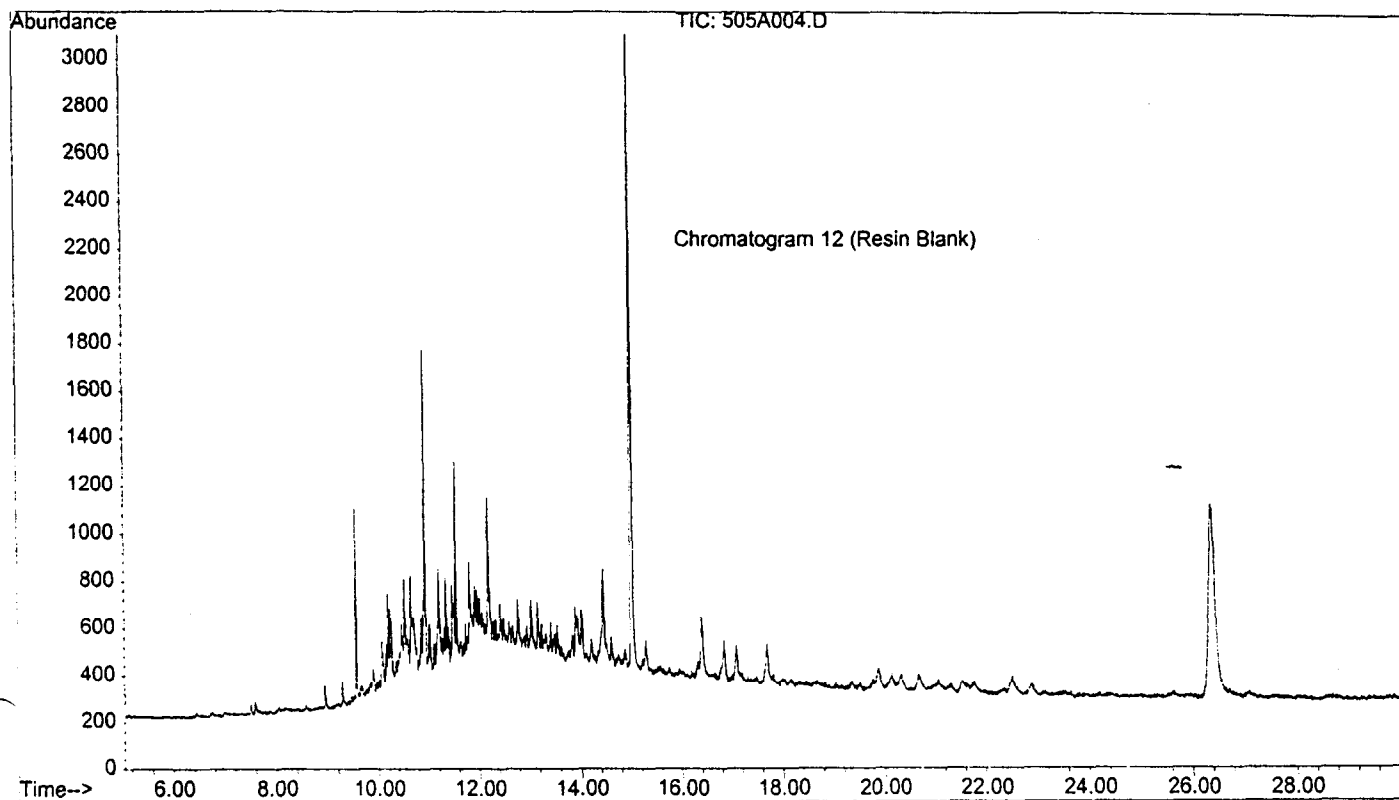
Chromatogram 10



File : M:\TAL\ARB97\THIMET\040297\402A003.D  
Operator : Matt Hengel  
Acquired : 2 Apr 97 5:54 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 50 pg/ul 3ul inj.  
Misc Info :  
Vial Number: 3

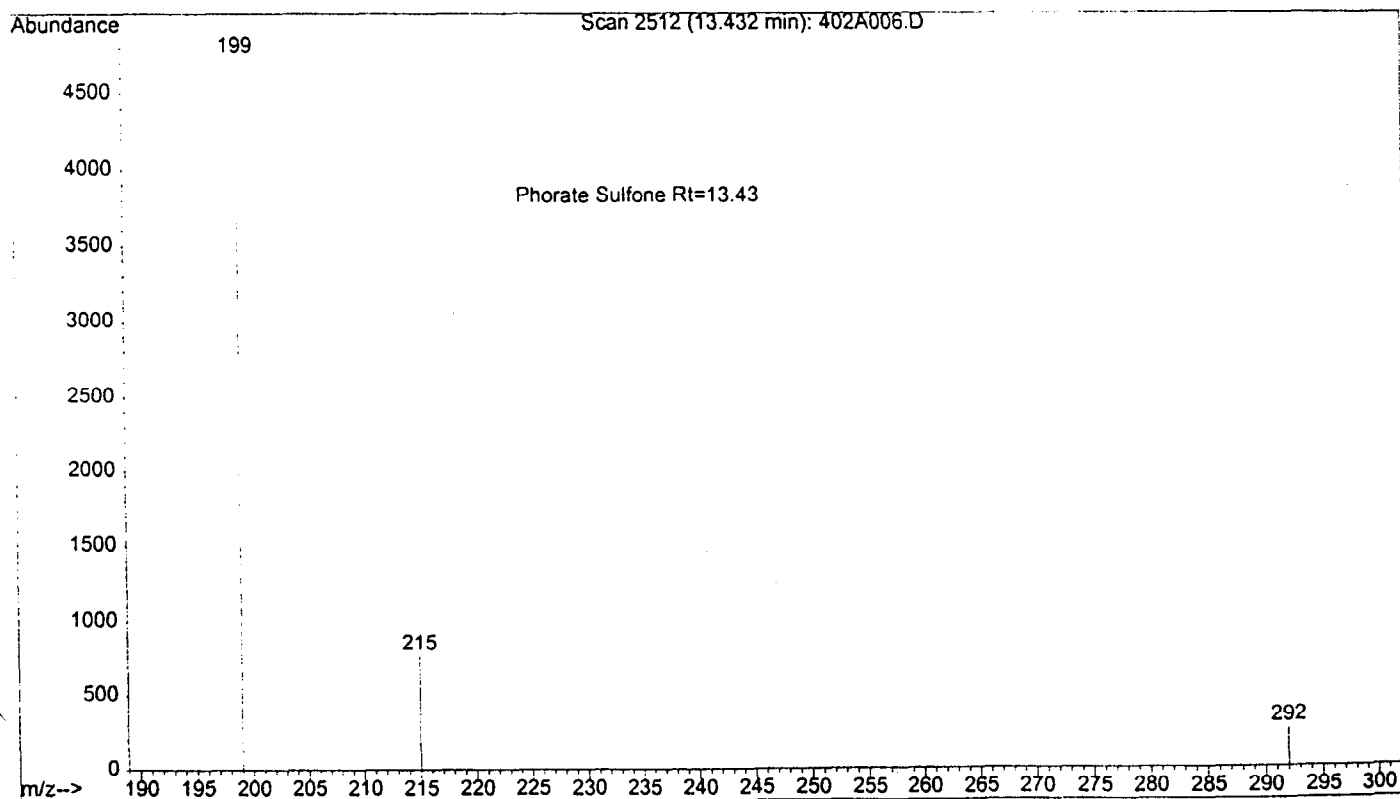
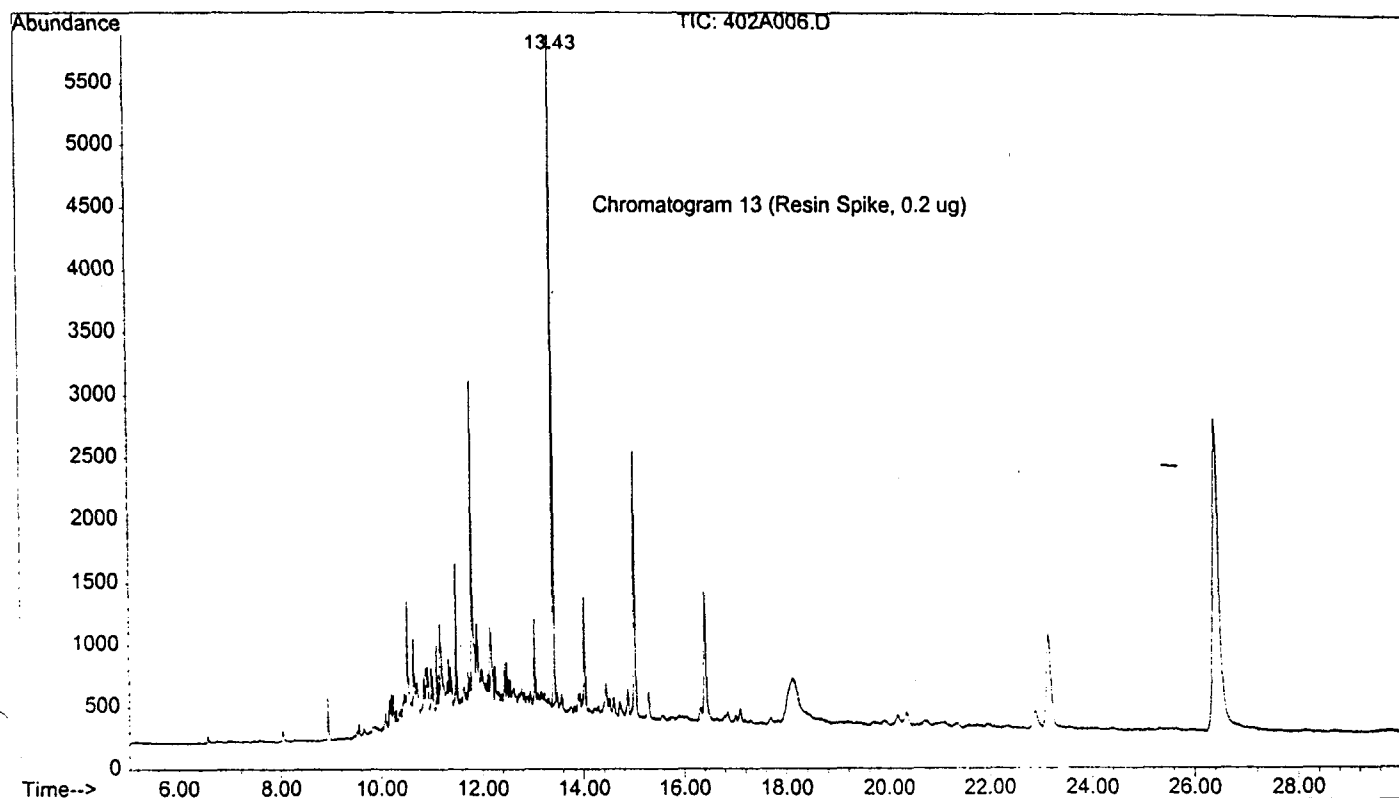


File : M:\TAL\ARB97\THIMET\050597\505A004.D  
Operator : Matt Hengel  
Acquired : 5 May 97 1:28 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 539C/2ml 3ul inj.  
Misc Info :  
Vial Number: 4

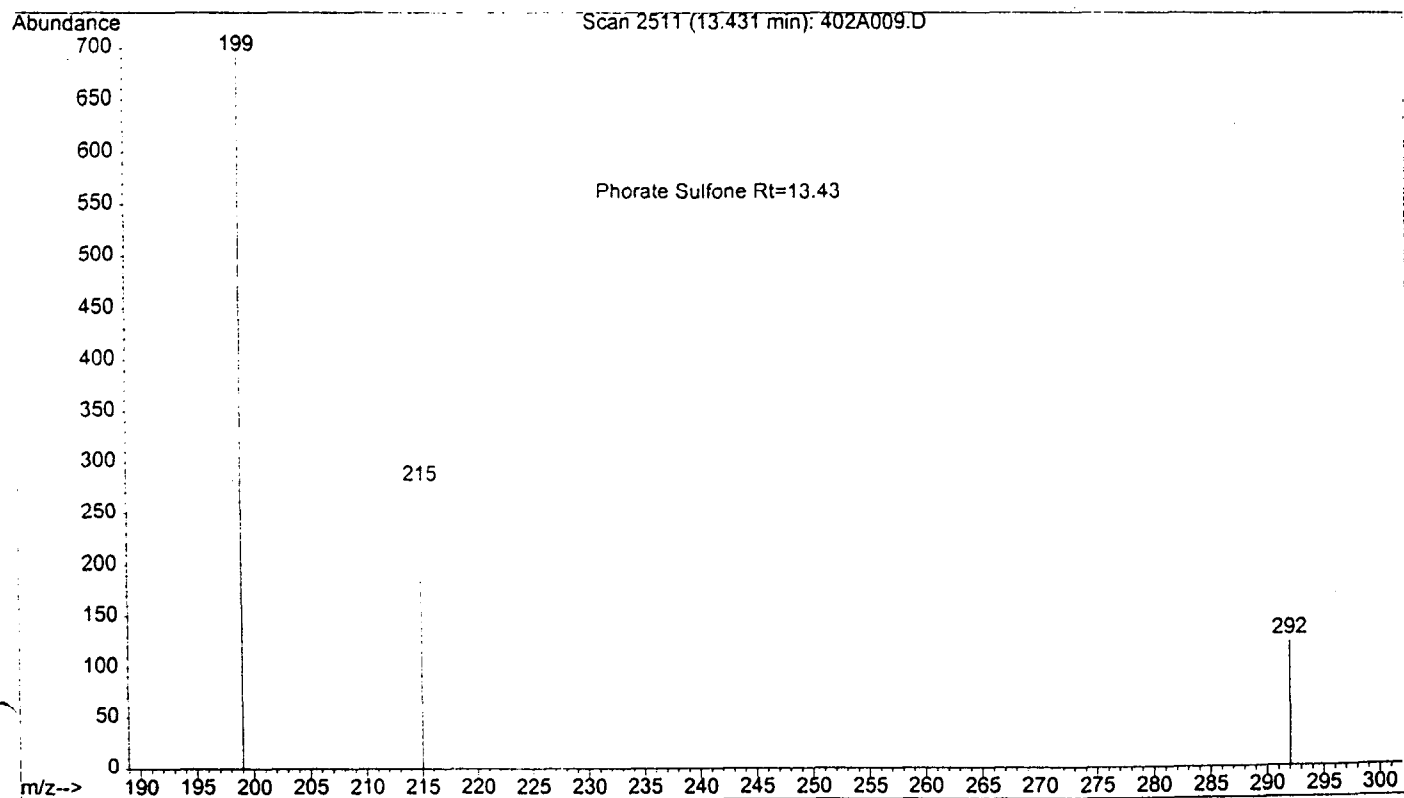
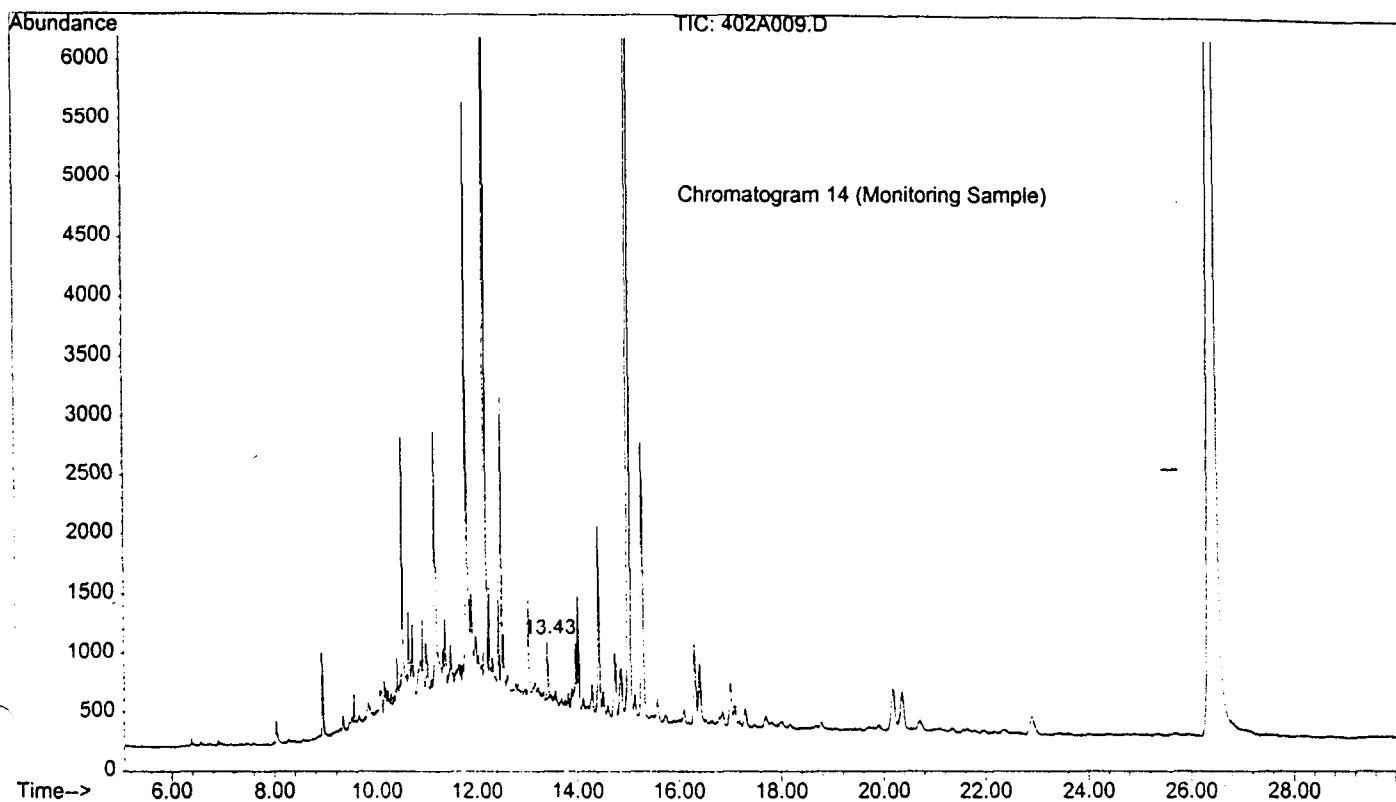




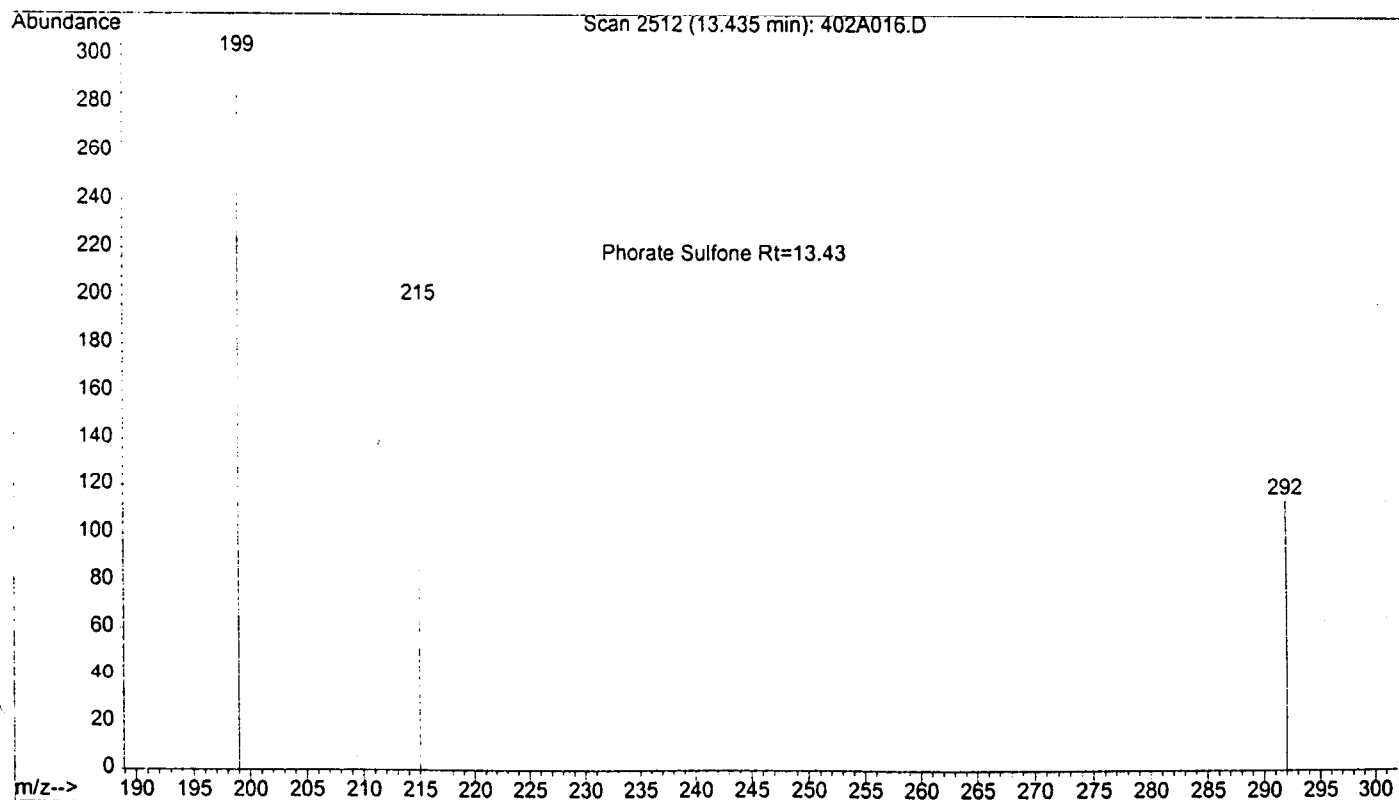
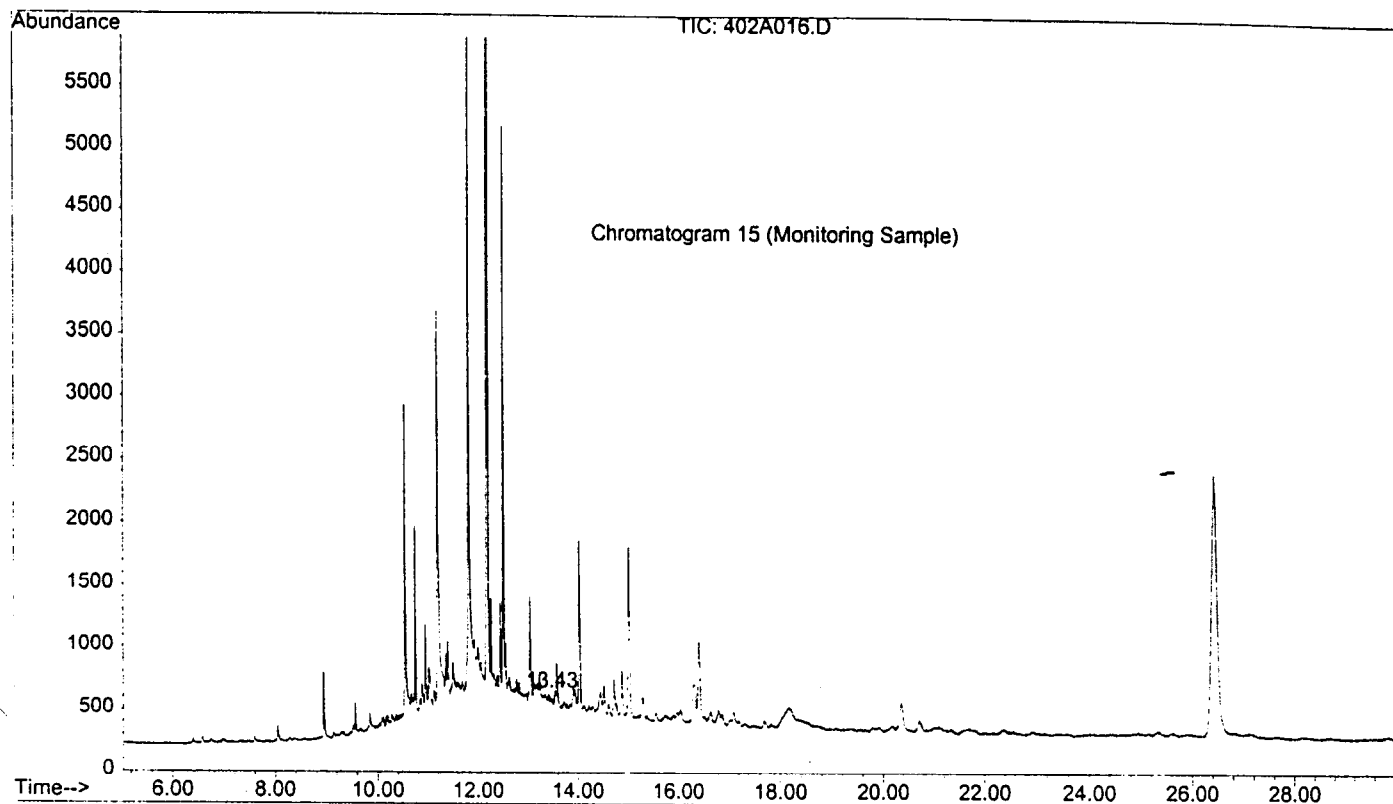
File : M:\TAL\ARB97\THIMET\040297\402A006.D  
Operator : Matt Hengel  
Acquired : 2 Apr 97 7:35 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 274MV0.2R2/2ml 3ul inj.  
Misc Info :  
Vial Number: 5



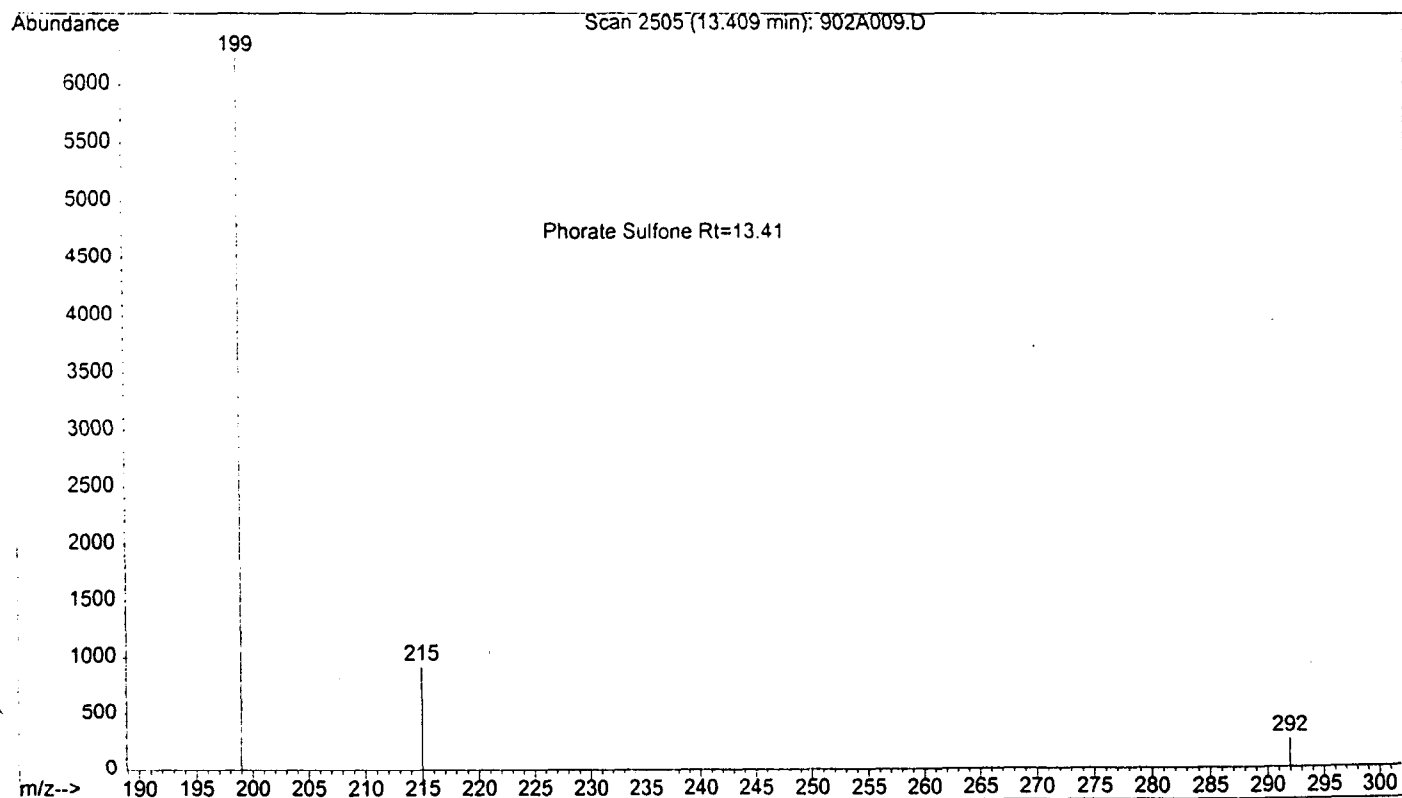
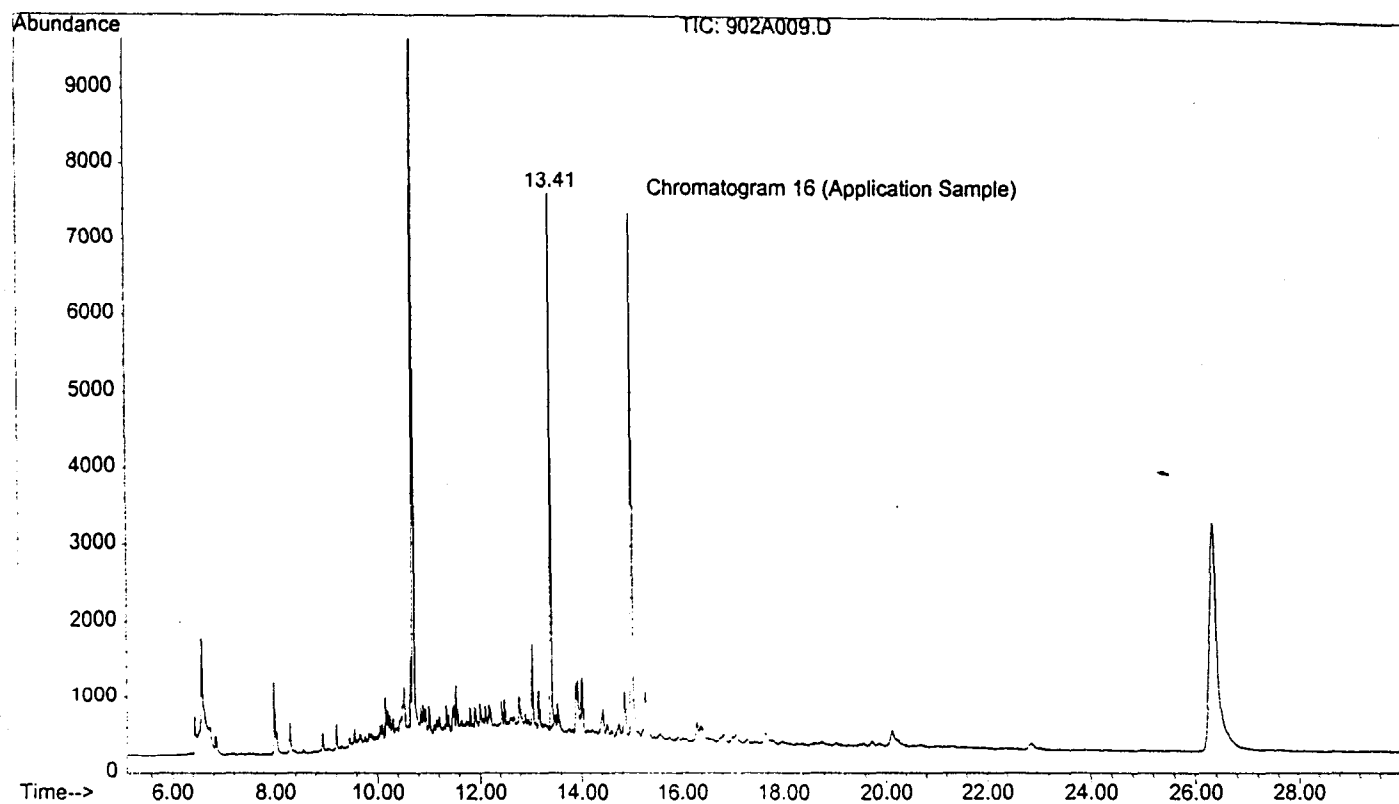
File : M:\TAL\ARB97\THIMET\040297\402A009.D  
Operator : Matt Hengel  
Acquired : 2 Apr 97 9:16 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 284(BOR-2)/2ml 3ul inj.  
Misc Info :  
Vial Number: 6



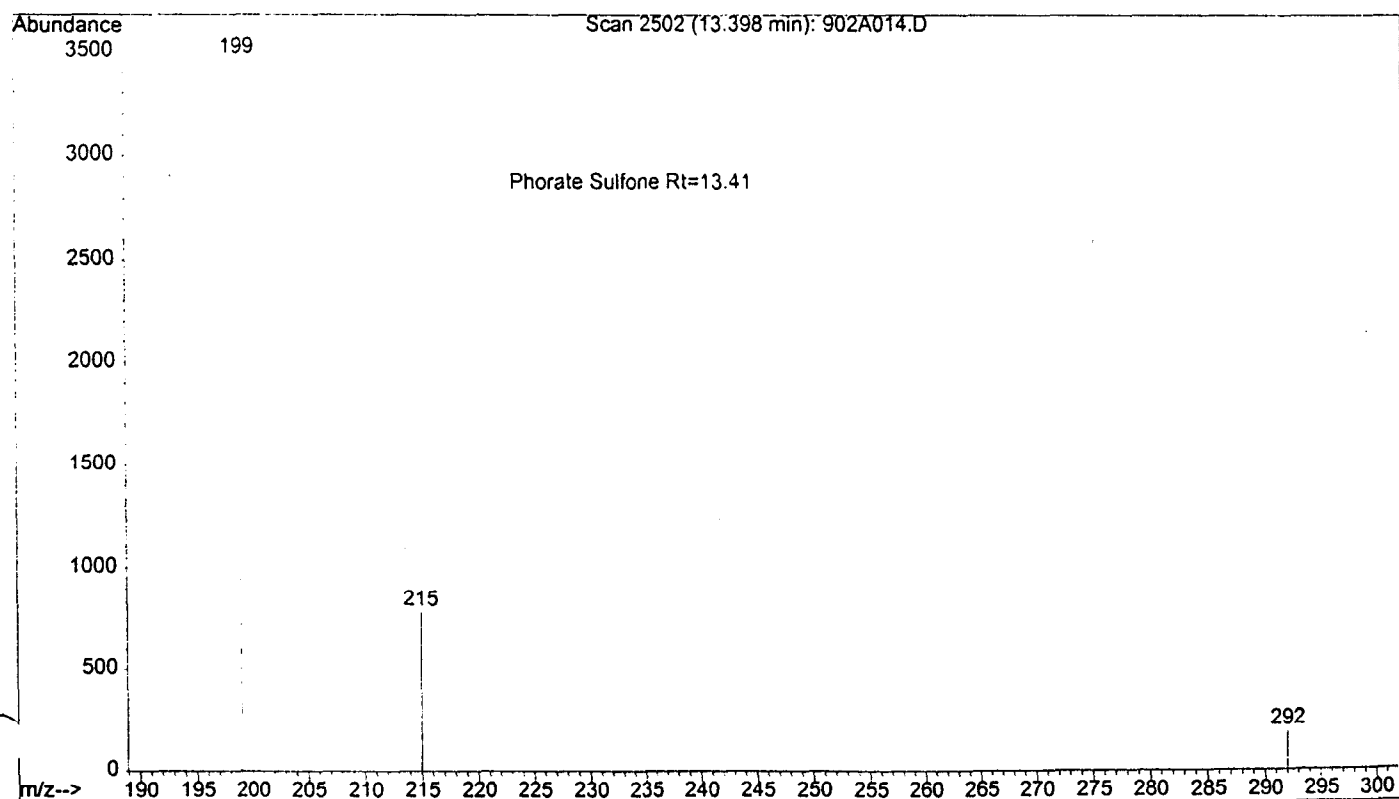
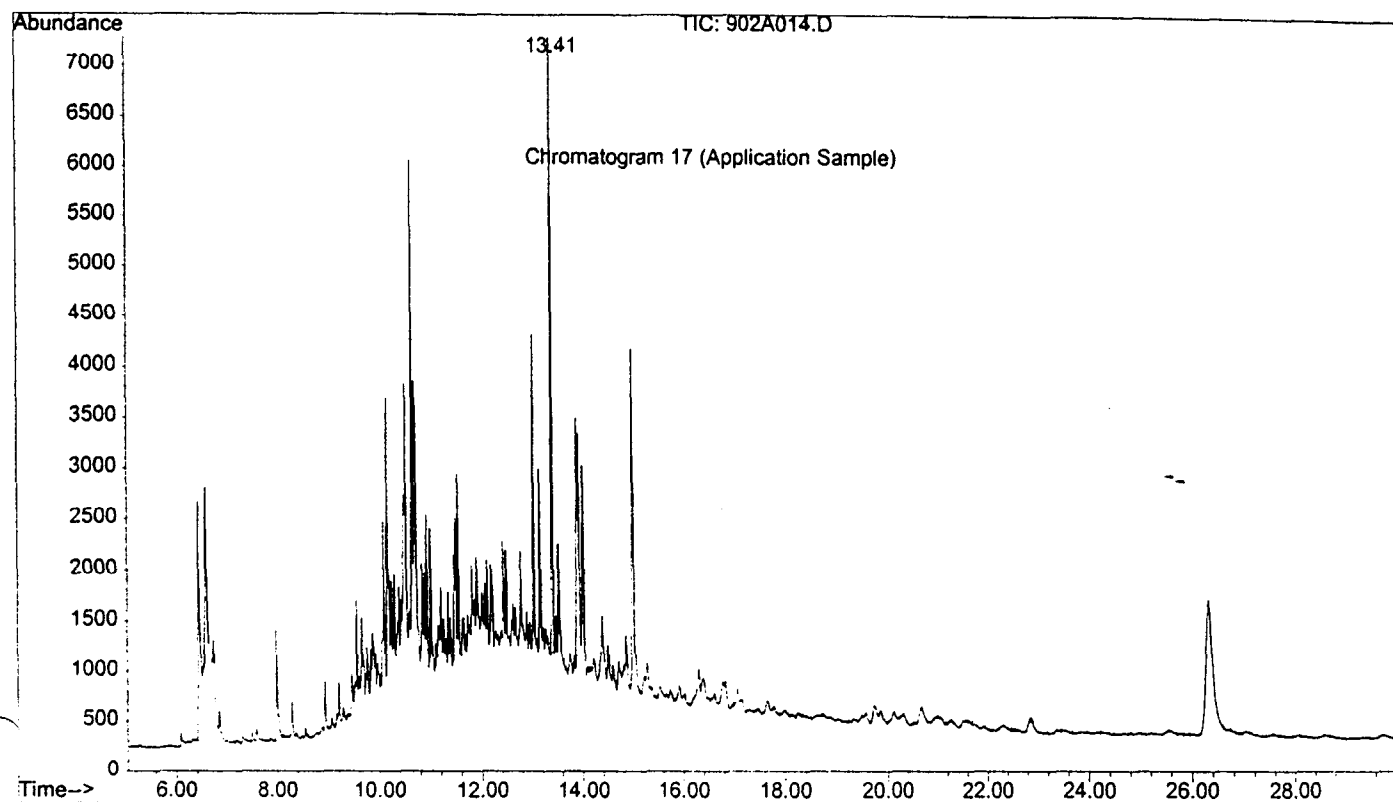
File : M:\TAL\ARB97\THIMET\040297\402A016.D  
Operator : Matt Hengel  
Acquired : 3 Apr 97 1:12 am using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 300(BOR-4)/2ml 3ul inj.  
Misc Info :  
Vial Number: 9



File : M:\TAL\ARB97\THIMET\090297\902A009.D  
Operator : Matt Hengel  
Acquired : 2 Sep 97 5:43 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 668 (E4)/2ml 3ul inj.  
Misc Info :  
Vial Number: 6



File : M:\TAL\ARB97\THIMET\090297\902A014.D  
Operator : Matt Hengel  
Acquired : 2 Sep 97 8:32 pm using AcqMethod PHORSUL  
Instrument : GC/MS Ins  
Sample Name: 670 (N5)/2ml 3ul inj.  
Misc Info :  
Vial Number: 8



APPENDIX III

PESTICIDE USE RECOMMENDATION  
AND REPORT

MONTH Aug 1 YEAR 97 2

☐ NURSERY 3

4. 22-27-08-0011

**BASE & MERIDIAN**

17

19

64

REVIEWED BY

Submit to Agricultural Commissioner within 10 days of month following application

33-017C (3/90)

**For Agency Use Only**

(1997)

APPLICATION - RESTRI

D MATERIALS - SUPPLEMENT

PERM

PAGE NO. 2 of 2

GN	by school	SEC	TWN	RNG	MAP ID	COMMODITY	ACRES/ UNITS	PESTICIDES	PESTS	F*	M**	RATE	DILUTION VOLUME	APPL	DATE/TIME
1.	St Westbrook Ln	26	18N	1W	33	Lulies	2	Methyl-Bromide/soil		g	gr	40#/acre			NOT
2.	Same - across St.	27	"	"	14		8	Thimet / nema		gr	gr	40#/acre			
10.	Cemetery Field	26	"	"	m-1		5								
11.															
12.	Oceanview Dr. / So E / sd.	22	"	"	364		10	Telone II / Soil organ		L	gr	35 gals/acre			
13.								Thimet / nema		gr	gr	40#/acre			
14.	Oceanview Dr.	22			364		10	metham sodium / soil organ		L	gr	25 gals/acre			
15.	Behind Shed	22			12		10	Thimet / nema		gr	gr	40#/acre			
16.	Sarward key barn	27			2019 -		9								
17.	1/4 mile W of Sarward key barn	27			30		6	Dizyston / aphids		g	gr	4-8#/acre			
18.	Cemetery	26			m-1		12								
19.	Westbrook Ln by school	26			33		10								
20.	Sarward / 1st St So.	27			2324		10								
21.	maris	26			m-67		5								
22.															
23.															
24.															
25.															
26.															
27.															
28.															
29.															
30.															
31.															
32.															
33.															
34.															

County 08

Section 27

Township 17 N

Range 1 W

BAREX MERIDIAN H

APPLICANT SIGNATURE

J. Westbrook

DATE

7-25-97

ISSUED BY

James O. Buckles

DATE

7-25-97

\* Formulation: L-Liquid B-Bait D-Dust F-Fumigant  
G-Granules WP-Wettable Powder O-Other

\*\* Method: A-Air F-Fumigation G-Ground O-Other



APPENDIX IV

DPR's  
MONITORING RECOMMENDATIONS FOR PHORATE

## Memorandum

To: George Lew, Chief  
Engineering and Laboratory Branch  
Monitoring and Laboratory Division  
Air Resources Board  
600 North Market Boulevard  
Sacramento, California 95812

Date: February 27, 1997

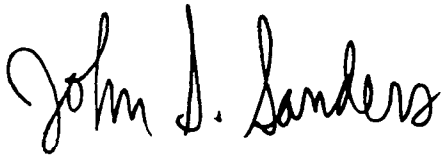
From: Department of Pesticide Regulation - 1020 N Street, Room 161  
Sacramento, California 95814-5624

Subject: AIR MONITORING RECOMMENDATION FOR PHORATE

Attached is the Department of Pesticide Regulation's (DPR) recommendation for monitoring the insecticide phorate. DPR provides this recommendation pursuant to the requirements of Assembly Bill 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5). DPR bases its air monitoring recommendations on historical phorate use information. Therefore, we request that you consult with the agricultural commissioner in the county where air monitoring will be conducted to select appropriate sites.

We anticipate submission of air monitoring data by September, 1998.

If you have any questions please contact Kevin Kelley, of my staff, at (916) 324-4187.



John S. Sanders, Chief  
Environmental Monitoring and  
Pest Management Branch  
(916) 324-4100

Attachment



George Lew  
March 3, 1997  
Page 2

cc: Daniel J. Merkley, Agricultural Commissioner Liaison (w/attachment)  
Ted Davis, Agricultural Commissioner Kern County (w/attachment)  
Raymond Menebroker - ARB (w/attachment)  
Kevin Mongar - ARB (w/attachment)  
Lynn Baker - ARB (w/attachment)  
Charles M. Andrews - DPR (w/attachment)  
Gary Patterson - DPR (w/attachment)  
Barry Cortez - DPR (w/attachment)  
John Donahue - DPR (w/attachment)  
Kevin Kelley DPR (w/attachment)  
Madeline Brattesani - DPR (w/attachment)



Staff Report

**USE INFORMATION AND AIR MONITORING  
RECOMMENDATION FOR THE PESTICIDE ACTIVE  
INGREDIENT PHORATE**

February 1997

Principal Author

**Kevin Kelley**  
Associate Environmental Research Scientist

State of California  
Department of Pesticide Regulation  
1020 N Street  
Sacramento, California 95814-5624

## **USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENT PHORATE**

### **A. BACKGROUND**

This recommendation contains general information regarding the physical-chemical properties and the historical trends in the use of O,O-Diethyl S-ethylmercaptomethyl dithiophosphonate (phorate). The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Phorate (CAS: 298-02-2) exists as clear liquid. Phorate has a molecular formula of  $C_7H_{17}O_2PS_3$  a formula weight of 260.40 g/mole, and a specific density of 1.156 at 25/4 °C. Phorate has a water solubility of 20 mg/L at 24 °C, a Henry's Constant of  $6.4 \times 10^{-6}$  atm · m<sup>3</sup>/mol at 20–24 °C, and a vapor pressure of  $8.4 \times 10^{-4}$  mm Hg at 20 °C. Phorate is miscible with carbon tetrachloride, vegetable oils, xylene, and various other organic solvents. The half-life ( $t_{1/2}$ ) of phorate is 96 hours at 25 °C and pH 7.0.

Phorate sulfoxide and phorate sulfone, and their phosphorothioate analogs are the major soil metabolites. Phorate sulfoxide, a microbial metabolite, may be further degraded to phorate oxon by soil-microorganisms. Purportedly, soil-type plays a larger role in phorate degradation than soil temperature or pH. Reported half-lives of phorate in loam or sandy soils are 82 days and 68 days respectively.

Exposure limits for phorate are: ACGIH TLV:TWA 0.05 mg/m<sup>3</sup> ppm, STEL 0.2mg/m<sup>3</sup>. Phorate's acute oral LD<sub>50</sub> for male and female rats is 3.7 and 1.6 mg/kg for rats. Its LC<sub>50</sub> (48 hour) is 5.4 µg/L for rainbow trout, and 1.8 µg/L for bluegill sunfish. Based on its low NOEL, phorate entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984).

### **B. USE OF PHORATE**

As of February 14, 1997, there were 7 phorate-containing products registered for use in California. The currently registered phorate products include: 1) four agricultural products (which may be referred to as thimet) for the control of mites, aphids, leafhoppers, thrips, Lygus bugs, leafminers, corn rootworms, wireworms, and other insect pests in beans, corn, cotton, potato, sorghum sugarbeets and wheat; 2) two 6.5% products (formulated with 6.5% Pentachloronitrobenzene), for the control of insects and fungi, on cotton; and 3) one home-use product (2% phorate) for control of thrips, bugs (Hemiptera), aphids and mites on ornamentals, tomatoes, roses and in and around home gardens. Agricultural products containing 15 or 20 % phorate AI have the Signal Word "Danger/Poison" on their labels. The home use product has the Signal Word "Warning" on the label.

When formulated for agricultural uses, phorate is a restricted material, and all use must be reported to the county agricultural commissioner in the county where it is applied. This information is forwarded to DPR, where it is compiled and published in an annual Pesticide Use Report (PUR). When formulated for home use, phorate is not a restricted material, and use is not reported to the county agricultural commissioner, nor to DPR. Therefore, information presented in this monitoring recommendation is based on agricultural uses of phorate. For purposes of this monitoring recommendation, historical use rates were calculated by dividing the total pounds of phorate applied (as reported in the PUR) by the acres to which it was applied.

Phorate is a widely-used, systemic organophosphate insecticide. In California's agricultural setting, phorate is a soil-applied pesticide which may be applied before planting, at cultivation following crop emergence, or as a side-dressing prior to the development of pest problems. Phorate is formulated as a granular formulation and may be soil incorporated, or incorporated into the soil by irrigation following application. Phorate is applied by ground based equipment.

According to the PUR, nearly 100% of all the agricultural applications of phorate occur in twelve counties (Table 1), with the greatest amounts applied in Fresno, Tulare, Kern and Kings counties. In Fresno and Tulare Counties, applications of phorate to cotton begin to rise in late March, and

**Table 1. Annual Agricultural Use of Phorate (Pounds of Active Ingredient)**

County	1993	1994	1995
Fresno	43,829.6	39,843.4	37,549.0
Tulare	28,237.3	33,884.4	28,424.6
Kern	18,977.4	24,875.1	10,530.1
Kings	16,789.3	15,057.1	14,305.3
Merced	6,538.1	4,848.6	6,936.5
Madera	6,192.6	3,792.7	3,906.9
Riverside	5,506.6	14,054.3	6,940.8
Sacramento	5,051.1	8,700.6	8,377.6
San Diego	3,988.8	1,178.8	851.1
San Joaquin	2,851.8	2,792.9	6,865.5
Del Norte	2,966.5	2,500.1	3,926.6
Imperial	2,769.2	6,482.0	4,475.1
County Totals	138,962.3	156,965.0	133,089.1
<i>Percent of Total</i>	<i>98.0</i>	<i>97.1</i>	<i>98.8</i>
<b>CALIFORNIA TOTAL</b>	<b>147,626.2</b>	<b>161,689.6</b>	<b>134,751.7</b>

taper off in early May, with the greatest amounts applied in April (Table 2). However, the averaged application rates in Tulare County are almost 1/2 lb. AI/acre greater than averaged application rates in Fresno County. Phorate applications in other counties (except Del Norte County) range from 0.5 to 2.5 lbs AI/acre but applications tend to be spread more evenly throughout the year, and consistency is lacking.

**Table 2. Applications of Phorate in Tulare and Fresno Counties in April to Cotton**

County - Month	1995		1994		1993	
	Lbs Used <sup>1</sup>	Rate <sup>2</sup>	Lbs Used <sup>1</sup>	Rate <sup>2</sup>	Lbs Used <sup>1</sup>	Rate <sup>2</sup>
<b>Tulare - April</b>	25,671.	1.3	26,993.	1.2	26,320.	1.2
	8		5		9	
<b>Fresno - April</b>	25,390.	0.9	21,709.	0.8	25,330.	0.8
	1		7		1	

<sup>1</sup> In pounds of active ingredient.

<sup>2</sup> Average rate (in pounds of active ingredient per acre) for month of use.

In Del Norte County, phorate is applied to nursery products from July through October, with occasional applications in November and December. Averaging application rates for these months showed that consistently high application rates are made during August, September and October (Table 3). Yearly averages, for these months were calculated and are presented in Table 3. Averaged application rates were 8.1, 8.6, and 9.5 lbs AI/acre for August, September and October, respectively. The next greatest (and consistent) rate of application ranges from 2.3 to 3.1 lbs AI/acre and occurs in several counties.

**Table 3. Averaged Monthly Rate of Phorate Use in Del Norte County for 1993 through 1995.**

Month	Commodity	lbs Applied	Acres	Rate
August	Nursery Products	1,879.5	230.9	8.1
September	Nursery Products	5,370.3	621.3	8.6
October	Nursery Products	2,009.3	211.9	9.5

<sup>1</sup> In pounds active ingredient per acre.

## **C. RECOMMENDATIONS**

### **1. *Ambient Air Monitoring***

The historical trends in phorate use suggest that monitoring should occur over a 30- to 45-day sampling period in Tulare County from late March through early May, with the bulk of the sampling conducted in April. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be located near cotton growing areas. Ambient samples should not be collected from samplers immediately adjacent to fields or orchards where phorate is being applied. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to phorate applications.

Replicate (collocated) samples are needed for five dates at each sampling location. Two collocated samplers (in addition to the primary sampler) should be run on those days. The dates chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Field blank and spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling.

### **2. *Application-Site Air Monitoring***

The historical trends in phorate use (Table 3) suggest that application-site air monitoring should be conducted during August, September, or October in Del Norte County where application rates are consistently high. Application rates to nursery commodities (cut flowers, field grown plants, etc.) range from range from 8.1 lbs AI/acre to 9.5 lbs AI/acre. Although phorate is not widely applied in Del Norte County during these months, care should still be taken so that nearby applications do not contaminate collected samples. A three day monitoring period should be established with sampling times as follows: application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of five samplers should be positioned, one on each side of the field, the fifth sampler should be collocated at one position. Background samplers should collect enough volume (either 12 hours at 15 liters/min., or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally, samplers should be placed a minimum of 20 meters from the field, however, wherever samplers are placed, the distance from the field must be reported. Field blank and field spike samples should be collected at the same environmental conditions (temperature humidity, exposure to sunlight) and experimental conditions (similar air flow rates) as those occurring at the time of sampling.

Additionally, we request that you provide in the monitoring report: 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover; and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North).



**APPENDIX V**

**APPLICATION AND AMBIENT FIELD LOG SHEETS**

# LOG BOOK

Project: Phorate Application Del Norte Co.  
Project #: C97-040

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
1	<del>PHORAP</del> NB	8/26/97	1715	Background #2	PC	KEM
		8/27	1720			
2	NFS1	8/26/97	1715	Field Spike A		
		8/27	1720			
3	WB	8/26/97	1720			
		8/27	1725			
4	WFS2	8/26/97	1720			
		8/27	1725	#10		
5	SR	8/26/97	1745			
		8/27	1730	#31		
6	SFS3	8/26/97	1745			
		8/27	1730	26		
7	EB	8/26/97	1755	Plan dropped slightly 2 units		
		8/27	1740	#19		
8	EFS4	8/26	1755	had wrong "top"; changed with the grass ambient		
		8/27	1740	#41		
9	PHORAPT B	8/27/97	1700	Trip Blank		
10	" " TS1	8/27	1700	Trip Spike		
11	TS2	8/27	1700			
12	TS3	8/27	1700			
13	TS4	8/27	1700			
14	PHORAPV1	8/27	1720		PC	
		8/27	1950			
15	W1	8/27	1725			
		8/27	2005			
16	S1	8/27	1730			
		8/27	1950			
17	E1	8/27	1740			
		8/27	2010	Roto A		
18	E10	8/27	1740	Duplicate #4		
		8/27	2010			
19	N2	8/27	1950			
		8-27	2005			
20	<del>W</del> 2	8/27	2005			
		8/27	2330			
21	S2	8/27	2000			
		8/27	2030			
22	E2	8/27	2010			
		8/27	2340			
23	E20	8/27	2010			
		6/27	2340			

changed pump & tree (A)

Start Appl.  
1740

# LOG BOOK

Project: Phorate Application Del Norte Co.  
Project #: C97-040

Log Number	Sample ID	Date	Time	Comments	weather	taken by
					o = overcast pc = partly cloudy k = clear	
24	N3	8/27	2325	1430 rain and morning stopped raining about 10:00 am	O	KEM
		8/28	<del>2325</del>			
25	W3	8/27	2330			
		8/28	1435			
26	S3	8/27	2335			
		8/28	1440			
27	E3	8/27	2340			
		8/28	1445			
28	E3D	8/27	2340			
		8/28	1445	pump was limit low at 0900		
		8/28	1450			
29	N4	8/28	2325			
		8/28	1435			
30	W4	8/28	2320			
		8/28	1440			
31	S4	8/28	2310			
		8/28	1445			
32	E4	8/28	2300			
		8/28	1445			
33	E4D	8-28	2300			
		8-28	2325			
34	N4	8-29	1708	N5	K	
		8-28	2320			
35	W4	8/29	1710	W5		
		8-28	2310			
36	S4	8/29	1715	S5		
		8-28	2300			
37	E4	8/29	1725	E5		
		8-28	2300			
38	E4D	8/29	1725	E5D		
		8/29	1705			
39	N5	8/29	2050	N6		
		8/29	1710			
40	W5	8/29	2055	W6		
		8/29	1715			
41	S5	8/29	2035	S6		
		8/29	1725			
42	E5	8/29	2030	E6		
		8/29	1725			
43	E5D	8/29	2030	E6D		
		8/29	2050			
44	N6	8/29	2050	N7		
		8/29	2055			
45	W6	8/30	1225	W7		

1445 Appl. #2  
Start

39  
40  
41  
42  
43  
44  
45

pump at 1.5 units low



**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

L.A.P.E.

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
1	SJ-1	3/24/97	1130	Primary ROTOMETER IS #1	K	L.J.
		3/25/97	1100			
2	HEL-1	3/24/97	1215	" " #24		
		3/25/97	1140			
3	FP-1	3/24/97	1235	" " #4		
		3/25/97	1205			
4	BOR-1	3/24/97	1330	" " #8		
		3/25/97	1245			
5	ARB-1	3/24/97	1445	" " #25		
		3/25/97	1430			
6	SJ-2	3/25/97	1100			
		3/26/97	0900			
7	HEL-2	3/25/97	1140			
		3/26/97	0935			
8	FP-2	3/25/97	1205			
		3/26/97	1005			
9	BOR-2	3/25/97	1245			
		3/26/97	1035			
10	ARB-2	3/25/97	1430			
		3/26/97	1405			
11	SJ-3	3/26/97	0900			
		3/27/97	0830			
12	SJ-3D	3/26/97	0900	DUPLICATE ROTOMETER IS #		
		3/27/97	0830			
13	HEL-3	3/26/97	0935			
		3/27/97	0845			
14	HEL-3D	3/26/97	0935	" " #29		
		3/27/97	0845			
15	FP-3	3/26/97	1005			
		3/27/97	0915			
16	FP-3D	3/26/97	1005	" " #23		
		3/27/97	0915			
17	BOR-3	3/26/97	1035			
		3/27/97	1000			
18	BOR-3D	3/26/97	1035	" " #9		
		3/27/97	1000			
19	ARB-3	3/26/97	1405			
		3/27/97	1200			
20	ARB-3D	3/26/97	1405	" " #26		
		3/27/97	1200			
21	B-3	3/26/97	1425	Blank DONE AT ARB SITE		
22	SJ-4	3/27/97	0830			
		3/28/97	0830			

**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
23	HEL-4	3/27/97	0845		K	L.J.
		3/28/97	0900			
24	FP-4	3/27/97	0915			
		3/28/97	0920			
25	BOR-4	3/27/97	1000			
		3/28/97	1000			
26	ARB-4	3/27/97	1200	sample was collected First ON 3/28/97	↓	↓
		3/28/97	0730			
27	SJ-5	3/31/97	1000		NORTH 20 NINE	LDT
		4-1-97	0930			
28	HEL-5	3/31/97	1030			
		4-1-97	1000			
29	FP-5	3/31/97	1100			
		4-1-97	1025			
30	BOR-5	3-31-97	1130			
		4-1-97	1050			
31	ARB-5	3-1-97	1330			
		4-1-97	1245			
32	SJ-6	4-1-97	0930		NORTH 35 YR	
		4-2-97	0915			
33	HEL-6	4-1-97	1000			
		4-2-97	0945			
34	FP-6	4-1-97	1025			
		4-2-97	1010			
35	BOR-6	4-1-97	1050			
		4-2-97	1100			
36	ARB-6	4-1-97	1245			
		4-2-97	1335			
37	SJ-7	4-2-97	0915			
		4-3-97	0900			
38	SJ-7D	4-2-97	0915			
		4-3-97	0915			
39	HEL-7	4-2-97	0945			
		4-3-97	1000			
40	HEL-7D	4-2-97	0945			
		4-3-97	1000			
41	FP-7	4-2-97	1010			
		4-3-97	1025			
42	FP-7D	4-2-97	1010			
		4-3-97	1025			
43	BOR-7	4-2-97	1100			
		4-3-97	1120			
44	BOR-7D	4-2-97	1100			
		4-3-97	1130			

**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
45	ARB-7	4-2-97	1335		K	LDT
		4-3-97	1330			
46	ARB-7D	4-2-97	1335			
		4-3-97	1330			
47	BLA-1-	4-2-97	0945	HELM School		
48	SJ-8	4-3-97	0910			
		4-4-97	0830			
49	HEL-8	4-3-97	1000			
		4-4-97	0905			
50	FP-8	4-3-97	1025			
		4-4-97	0930			
51	BCP-8	4-3-97	30			
		4-4-97	1000			
52	APB-8	4-3-97	1330			
		4-4-97	1200			
53	SS-9	4-7-97	0800		K	DR
		4-8-97	0930			
54	HEL-9	4-7-97	0815		L	J
		4-8-97	0950			
55	FP-9	4-7-97	0830		L	J
		4-8-97	1010			
56	BOR-9	4-7-97	0900		L	J
		4-8-97	1035			
57	ARB-9	4-7-97	1110			
		4-8-97	730			
58	SS-10	4-8-97	0930			
		4-9-97	0915			
59	HEL-10	4-8-97	0950			
		4-9-97	0930			
60	FD-10	4-8-97	1010			
		4-9-97	1005			
61	BOR-10	4-8-97	1035			
		4-9-97	1035			
62	ARB-10	4-8-97	1230			
		4-9-97	1225			
63	SS-11	4-9-97	0915			
		4-10-97	0920			
64	SS-11D	4-9-97	0915			
		4-10-97	0910			
65	HEL-11	4-9-97	0930			
		4-10-97	0945			
66	HEL-11D	4-9-97	0930			
		4-10-97	0945			

**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by
67	FP-11	4-9-97	1005		C. L. T. by DR
		4-10-97	1010		
68	FP-11	4-9-97	1005		J L
		4-10-97	1010		
69	BOR-11	4-9-97	1030		J L
		4-10-97	1035		
70	BOR-11	4-9-97	1030		J L
		4-10-97	1035		
71	FP-11	4-9-97	1225		
		4-10-97	1250		
72	ARB-11	4-9-97	1225		
		4-10-97	1250		
73	SS-12	4-10-97	0920		
		4-11-97	0900		
74	HEL-12	4-10-97	0945		
		4-11-97	0925		
75	FP-12	4-10-97	1010		
		4-11-97	0945		
76	BOR-12	4-10-97	1035		
		4-11-97	1010		
77	ARB-12	4-10-97	1250		
		4-11-97	1140		
78	Blank	4-11-97	0900	San Joaquin School	
79	SJ-13	4-14-97	1120		
		4-15-97	0945		
80	HEL-13	4-14-97	1120		
		4-15-97	1015		
81	FP-13	4-14-97	1140	PUMP WAS OFF TIME UNKNOWN	
		4-15-97	1035	CIRCUIT BREAKER OFF	
82	BOR-13	4-14-97	1215		
		4-15-97	1105		
83	ARB-13	4-14-97	1425		
		4-15-97	1300		
84	FS-1	4-14-97	1425	FIELD SPIKE ROTO 26	
		4-15-97	1300	ARB SITE	
85	SJ-14	4-15-97	0945		
		4-16-97	0935		
86	HEL-14	4-15-97	1015		
		4-16-97	1000		
87	FP-14	4-15-97	1035		
		4-16-97	1025		
88	BOR-14	4-15-97	1105		
		4-16-97	1055		



**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
89	ARB-14	4-15-97 4-16-97	1300 1320			2.0.
90	FS-3	4-15-97 4-16-97	1300 1320	ARB SITE FIELD SPIKE ROTO 26		
91	SJ-15	4-16-97 4-17-97	0935 0920			
92	SJ-15D	4-16-97 4-17-97	0935 0920	DUPLICATE		
93	HEL-15	4-16-97 4-17-97	1000 0940			
94	HEL-15D	4-16-97 4-17-97	1000 0940	DUPLICATE		
95	FP-15	4-16-97 4-17-97	1025 1005	CIRCUIT BREAKER WAS OFF FOR THE 2ND TIME		
96	FP-15D	4-16-97 4-17-97	1025 1005	" DUPLICATE		
97	B-15	4-16-97 -	1025 -	WESTSIDE BLANK ELEMENTRY		
98	BOR-15	4-16-97 4-17-97	1055 1040			
99	BOR-15D	4-16-97 4-17-97	1055 1040	DUPLICATE		
100	ARB-15	4-16-97 4-17-97	1320 1240			
101	ARB-15D	4-16-97 4-17-97	1320 1240	DUPLICATE		
102	SJ-16	4-17-97 4-18-97	0925 0850			
103	HEL-16	4-17-97 4-18-97	0940 0905			
104	FP-16	4-17-97 4-18-97	1005 0915			
105	BOR-16	4-17-97 4-18-97	1040 0945			
106	ARB-16	4-17-97 4-18-97	1240 0740			
107	SS-17	4-21-97 4-22-97	0815 0915		PC	DR
108	HEL-17	4-21-97 4-22-97	0335 0935		↓	↓
109	FP-17	4-21-97 4-22-97	0850 0950			
110	BOR-17	4-21-97 4-22-97	0905 1010			

**LOG BOOK**  
Project: Phorate Ambient  
Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
111	ARB-17	4-21-97	1040			
		4-22-97	1140			DR
112	SS-18	4-22-97	0915			
		4-23-97	0920			
113	HEL-18	4-22-97	0935			
		4-23-97	0935			
114	FP-18	4-22-97	0950			
		4-23-97	1000			
115	BOR-18	4-22-97	1010			
		4-23-97	1020			
116	ARB-18	4-22-97	1140			
		4-23-97	150			
117	SS-19	4-23-97	0920			
		4-24-97	0920			
118	SS-19D	4-23-97	0920			
		4-24-97	0920			
119	HEL-19	4-23-97	0935			
		4-24-97	0935			
120	HEL-19D	4-23-97	0935			
		4-24-97	0935			
121	FP-19	4-23-97	1000			
		4-24-97	0950			
122	FP-19D	4-23-97	1000			
		4-24-97	0950			
123	BOR-19	4-23-97	1020			
		4-24-97	1020			
124	BOR-19D	4-23-97	1020			
		4-24-97	1020			
125	ARB-19	4-23-97	1150			
		4-24-97	1215			
126	ARB-19D	4-23-97	1150			
		4-24-97	1215			
127	SS-20	4-24-97	0920			
		4-25-97	0925			
128	HEL-20	4-24-97	0935			
		4-25-97	0940			
129	FP-20	4-24-97	0950			
		4-25-97	0900			
130	BOR-20	4-24-97	1020			
		4-25-97	0915			
131	ARB-20	4-24-97	1215			
		4-25-97	1050			
132	Blank	4-25-97	0915	Burrell Elementary		

**LOG BOOK**  
 Project: Phorate Ambient  
 Project #: C97-002

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear   taken by	
133	SJ-21	4-28-97	0910		K	DR
		4-29-97	0930			
134	HEL-21	4-28-97	0930			
		4-29-97	0950			
135	FP-21	4-28-97	0940			
		4-29-97	1005			
136	BOR-21	4-28-97	1000			
		4-29-97	1025			
137	ARB-21	4-28-97	1125			
		4-29-97	1200			
138	SJ-22	4-29-97	0930			
		4-30-97	0830			
139	HEL-22	4-29-97	0850			
		4-30-97	0850			
140	FP-22	4-29-97	1005			
		4-30-97	0905			
141	BOR-22	4-29-97	0925			
		4-30-97	0925			
142	ARB-22	4-29-97	1200			
		4-30-97	1055			
143	SJ-23	4-30-97	0830			
		5-1-97	0830			
144	SJ-23D	4-30-97	0830			
		5-1-97	0830			
145	HEL-23	4-30-97	0850			
		5-1-97	0850			
146	HEL-23D	4-30-97	0850			
		5-1-97	0850			
147	FP-23	4-30-97	0905	Power to pump off		
		5-1-97	0905			
148	FP-23D	4-30-97	0905	" "		
		5-1-97	0905			
149	BOR-23	4-30-97	0925			
		5-1-97	0935			
150	BOR-23D	4-30-97	0925			
		5-1-97	0935			
151	ARB-23	4-30-97	1055			
		5-1-97	1120			
152	ARB-23D	4-30-97	1055			
		5-1-97	1120			
153	SJ-24	5-1-97	0830			
		5-2-97	0810			
154	HEL-24	5-1-97	0850			
		5-7-97	0825			



APPENDIX VI

PHORATE APPLICATION METEOROLOGICAL DATA

### Wind Speed and Direction at the Crescent City Airport

	26-Aug		27-Aug		28-Aug		29-Aug		30-Aug	
Hour	Wind Direction (degrees oriented to geo. N)	Wind Speed (knots)	Wind Direction (degrees oriented to geo. N)	Wind Speed (knots)	Wind Direction (degrees oriented to geo. N)	Wind Speed (knots)	Wind Direction (degrees oriented to geo. N)	Wind Speed (knots)	Wind Direction (degrees oriented to geo. N)	Wind Speed (knots)
12:00 AM	150	8	160	6	150	7	calm	calm	calm	calm
1:00 AM	150	11	130	5	150	8	calm	calm	120	3
2:00 AM	100	3	110	4	150	7	340	5	110	4
3:00 AM			140	4	130	5	360	4	calm	calm
4:00 AM	160	10	160	5	120	3	20	4	100	5
5:00 AM	160	11	160	5	100	4	350	3	100	6
6:00 AM	160	14			120	3	350	6	100	4
7:00 AM	180	16	110	4	calm	calm	350	7	100	5
8:00 AM	190	8	120	7	350	4	320	8	90	5
9:00 AM	170	8	170	10	30	6	340	8	100	6
10:00 AM	160	11	170	8	160	3	310	12	180	5
11:00 AM	150	11					300	12	190	5
12:00 PM			170	10	160	7	300	9	190	5
1:00 PM	130	11	170	8	180	10	320	11	200	9
2:00 PM	160	8	170	8	160	7				
3:00 PM	180	10	140	6	160	6	310	14		
4:00 PM	170	11	110	5	160	8				
5:00 PM							310	12		
6:00 PM	170	8			300	3				
7:00 PM	160	7	140	4	340	3	220	3		
8:00 PM	160	6	160	6	10	3	calm	calm		
9:00 PM	150	5	160	6	calm	calm	calm	calm		
10:00 PM			150	6	calm	calm	calm	calm		
11:00 PM	160	6	180	6	calm	calm	calm	calm		

**Phorate Application Meteorological Data (15 min. averages)**

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	238	1735	68.7	1013	83.5
1997	238	1750	68.7	1013	85.3
1997	238	1805	68.7	1013	86.0
1997	238	1820	69.1	1013	83.4
1997	238	1835	68.5	1013	84.5
1997	238	1850	69.5	1013	83.9
1997	238	1905	69.6	1013	83.7
1997	238	1920	69.1	1013	82.4
1997	238	1935	68.5	1013	83.9
1997	238	1950	67.8	1013	87.1
1997	238	2005	67.0	1013	89.8
1997	238	2020	66.5	1014	92.4
1997	238	2035	66.1	1014	93.1
1997	238	2050	65.4	1014	95.0
1997	238	2105	64.6	1014	97.3
1997	238	2120	64.4	1014	97.7
1997	238	2135	64.4	1014	97.7
1997	238	2150	64.0	1014	99.3
1997	238	2205	63.6	1014	99.4
1997	238	2220	62.8	1014	100.7
1997	238	2235	62.4	1014	102.1
1997	238	2250	62.2	1014	102.9
1997	238	2305	61.7	1014	103.1
1997	238	2331	61.5	1014	103.1
1997	238	2346	61.7	1014	103.2
1997	239	1	61.9	1014	102.0
1997	239	16	61.7	1014	101.6
1997	239	31	61.0	1014	102.6
1997	239	46	60.4	1014	103.0
1997	239	101	60.0	1014	103.1
1997	239	116	59.8	1014	103.4
1997	239	131	59.6	1014	103.3
1997	239	146	59.6	1014	103.1
1997	239	201	59.7	1014	102.7
1997	239	216	59.6	1014	102.1
1997	239	241	70.8	947	99.5
1997	239	256	59.1	1014	102.1
1997	239	311	58.9	1014	102.1
1997	239	326	58.5	1014	102.8
1997	239	341	58.3	1014	102.6
1997	239	356	58.0	1014	102.9
1997	239	411	58.0	1014	102.5
1997	239	426	57.9	1014	102.4

# Phorate Application Meteorological Data (15 min. averages)

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	239	441	57.8	1014	102.5
1997	239	456	57.8	1014	102.1
1997	239	511	58.1	1014	102.2
1997	239	536	89.6	947	99.5
1997	239	551	57.9	1014	101.3
1997	239	606	57.8	1014	98.9
1997	239	621	57.3	1014	97.4
1997	239	636	57.5	1014	97.7
1997	239	651	57.6	1014	98.1
1997	239	706	58.2	1014	101.2
1997	239	721	58.5	1014	98.8
1997	239	736	59.1	1014	96.1
1997	239	751	59.2	1014	98.3
1997	239	806	59.9	1015	99.7
1997	239	821	63.0	1015	97.1
1997	239	836	63.7	1015	93.2
1997	239	851	65.7	1015	90.6
1997	239	906	66.7	1015	86.0
1997	239	921	69.3	1015	84.2
1997	239	936	69.8	1015	81.1
1997	239	951	70.7	1015	77.8
1997	239	1006	69.8	1015	78.8
1997	239	1021	71.3	1015	79.1
1997	239	1036	70.7	1015	80.1
1997	239	1051	71.4	1015	81.4
1997	239	1106	72.6	1015	77.4
1997	239	1121	71.6	1015	79.0
1997	239	1136	71.6	1015	77.8
1997	239	1151	72.0	1015	75.4
1997	239	1206	71.1	1015	80.3
1997	239	1221	70.5	1015	83.3
1997	239	1236	70.8	1015	80.1
1997	239	1251	71.4	1015	79.6
1997	239	1306	71.2	1015	79.6
1997	239	1321	71.8	1015	78.0
1997	239	1336	71.3	1015	77.0
1997	239	1351	70.6	1015	79.3
1997	239	1406	71.0	1015	78.3
1997	239	1421	70.3	1015	81.4
1997	239	1436	70.4	1015	82.7
1997	239	1451	70.8	1015	80.5
1997	239	1506	70.0	1015	83.9
1997	239	1521	69.6	1015	86.8



# Phorate Application Meteorological Data (15 min. averages)

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	239	1536	68.3	1015	88.7
1997	239	1551	67.9	1015	89.3
1997	239	1606	68.1	1015	90.3
1997	239	1621	68.5	1015	87.8
1997	239	1636	69.7	1014	86.3
1997	239	1651	70.9	1014	84.9
1997	239	1706	70.3	1014	82.5
1997	239	1721	69.2	1014	82.8
1997	239	1736	69.9	1014	82.7
1997	239	1751	68.7	1014	84.6
1997	239	1806	68.8	1014	84.9
1997	239	1821	68.3	1014	84.1
1997	239	1836	68.3	1014	85.8
1997	239	1851	70.5	1014	83.2
1997	239	1906	69.8	1014	83.3
1997	239	1921	68.3	1014	82.4
1997	239	1936	66.6	1014	85.0
1997	239	1951	65.6	1014	89.7
1997	239	2006	65.2	1014	90.8
1997	239	2021	64.1	1014	92.2
1997	239	2036	63.5	1014	93.2
1997	239	2051	62.7	1014	95.4
1997	239	2106	62.3	1014	97.7
1997	239	2121	61.9	1014	98.6
1997	239	2136	62.0	1014	97.7
1997	239	2151	61.7	1014	97.6
1997	239	2206	61.1	1014	98.8
1997	239	2221	60.9	1014	97.8
1997	239	2236	60.9	1014	98.4
1997	239	2251	60.6	1014	98.3
1997	239	2306	60.5	1013	97.6
1997	239	2321	60.4	1013	96.9
1997	239	2336	60.0	1013	97.6
1997	239	2351	60.0	1013	97.8
1997	240	6	59.8	1013	98.2
1997	240	21	59.7	1013	98.2
1997	240	36	59.6	1013	97.8
1997	240	51	59.4	1013	98.3
1997	240	106	59.4	1013	98.2
1997	240	121	59.5	1013	98.0
1997	240	136	59.4	1013	98.3
1997	240	151	59.5	1013	97.7
1997	240	206	59.6	1013	97.6

**Phorate Application Meteorological Data (15 min. averages)**

<b>Year</b>	<b>Julian Date</b>	<b>Time</b>	<b>Temp. (F)</b>	<b>Barometric Pressure (hPa)</b>	<b>Relative Humidity</b>
1997	240	221	59.7	1013	97.3
1997	240	236	59.9	1013	96.9
1997	240	251	59.4	1013	97.7
1997	240	306	59.0	1013	97.9
1997	240	321	58.7	1013	99.0
1997	240	336	59.0	1013	98.0
1997	240	351	59.0	1013	97.4
1997	240	406	59.1	1013	96.8
1997	240	421	58.9	1013	97.1
1997	240	436	59.1	1013	96.7
1997	240	451	59.1	1013	96.3
1997	240	506	59.2	1013	96.2
1997	240	521	59.3	1013	96.1
1997	240	536	59.4	1013	95.6
1997	240	551	59.4	1013	95.3
1997	240	606	59.5	1013	95.3
1997	240	621	59.6	1013	94.9
1997	240	636	60.0	1013	94.4
1997	240	651	60.3	1013	94.1
1997	240	706	60.3	1013	93.9
1997	240	721	60.9	1013	93.6
1997	240	736	61.3	1013	92.7
1997	240	751	61.2	1013	93.8
1997	240	806	61.4	1013	94.1
1997	240	821	61.6	1013	94.6
1997	240	836	61.7	1014	94.2
1997	240	851	61.6	1014	94.9
1997	240	906	61.2	1014	97.4
1997	240	921	61.3	1014	95.2
1997	240	936	61.2	1014	96.6
1997	240	951	62.2	1014	95.3
1997	240	1006	63.3	1014	93.1
1997	240	1021	64.4	1014	91.6
1997	240	1036	65.3	1014	90.5
1997	240	1051	66.7	1014	84.6
1997	240	1106	66.9	1014	82.3
1997	240	1121	65.8	1015	86.8
1997	240	1136	66.7	1014	88.4
1997	240	1151	68.1	1015	85.3
1997	240	1206	68.0	1015	86.6
1997	240	1221	64.7	1015	94.0
1997	240	1236	64.4	1015	95.0
1997	240	1251	65.4	1015	93.8

# Phorate Application Meteorological Data (15 min. averages)

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	240	1306	65.4	1015	94.0
1997	240	1321	65.2	1015	94.6
1997	240	1336	65.9	1015	94.2
1997	240	1351	66.6	1015	91.3
1997	240	1406	67.6	1015	90.1
1997	240	1421	67.9	1015	90.0
1997	240	1436	68.8	1015	88.0
1997	240	1451	69.8	1015	87.7
1997	240	1506	69.9	1015	85.5
1997	240	1521	68.8	1015	88.3
1997	240	1536	68.2	1015	88.9
1997	240	1551	68.6	1015	88.6
1997	240	1606	69.0	1015	89.7
1997	240	1621	70.3	1015	86.3
1997	240	1636	69.8	1015	86.0
1997	240	1651	69.5	1015	85.4
1997	240	1706	69.4	1015	86.1
1997	240	1721	67.9	1014	87.6
1997	240	1736	67.4	1014	89.1
1997	240	1751	66.7	1014	90.6
1997	240	1806	66.6	1014	91.6
1997	240	1821	66.3	1014	92.1
1997	240	1836	66.1	1014	92.8
1997	240	1851	65.9	1014	93.1
1997	240	1906	65.7	1014	93.8
1997	240	1921	65.6	1014	94.0
1997	240	1936	65.6	1014	94.5
1997	240	1951	65.1	1014	95.0
1997	240	2006	64.8	1014	95.4
1997	240	2021	64.8	1014	96.0
1997	240	2036	65.0	1014	96.1
1997	240	2051	64.7	1014	96.4
1997	240	2106	64.6	1014	96.3
1997	240	2121	64.6	1014	97.2
1997	240	2136	64.3	1014	98.7
1997	240	2151	64.2	1014	98.6
1997	240	2206	64.1	1014	98.1
1997	240	2221	64.1	1014	97.7
1997	240	2236	63.8	1014	98.6
1997	240	2251	63.6	1014	99.6
1997	240	2306	63.3	1014	100.5
1997	240	2321	63.2	1014	100.9
1997	240	2336	63.2	1014	100.4

# Phorate Application Meteorological Data (15 min. averages)

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	240	2351	63.3	1014	99.6
1997	241	6	63.2	1014	99.9
1997	241	21	63.2	1014	99.7
1997	241	36	63.3	1014	99.0
1997	241	51	63.1	1014	99.2
1997	241	106	62.7	1014	100.4
1997	241	121	62.0	1013	101.4
1997	241	136	61.5	1013	101.7
1997	241	151	61.3	1013	102.7
1997	241	206	61.3	1013	102.7
1997	241	221	61.4	1013	102.7
1997	241	236	61.6	1013	101.5
1997	241	251	61.5	1013	102.1
1997	241	306	61.3	1013	102.6
1997	241	321	61.1	1013	102.3
1997	241	336	61.1	1013	102.6
1997	241	351	61.1	1013	102.7
1997	241	406	61.2	1013	103.2
1997	241	421	61.4	1013	103.0
1997	241	436	61.6	1013	102.8
1997	241	451	61.7	1013	102.2
1997	241	506	61.9	1013	101.0
1997	241	521	62.1	1013	101.0
1997	241	536	62.1	1013	101.4
1997	241	551	62.0	1013	101.6
1997	241	606	61.6	1013	101.5
1997	241	621	61.0	1013	102.3
1997	241	636	59.7	1013	103.3
1997	241	651	58.9	1013	103.8
1997	241	706	59.4	1013	104.1
1997	241	721	59.7	1013	104.1
1997	241	736	60.4	1013	103.7
1997	241	751	61.0	1013	103.1
1997	241	806	61.8	1013	102.5
1997	241	821	62.7	1013	100.8
1997	241	836	63.9	1013	96.7
1997	241	851	64.7	1013	95.6
1997	241	906	65.8	1013	94.7
1997	241	921	67.2	1013	92.9
1997	241	936	67.3	1013	93.4
1997	241	951	66.8	1013	93.6
1997	241	1006	66.8	1013	93.1
1997	241	1021	68.0	1013	91.9

# Phorate Application Meteorological Data (15 min. averages)

Year	Julian Date	Time	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity
1997	241	1036	68.0	1013	91.9
1997	241	1051	68.7	1013	90.7
1997	241	1106	67.7	1013	91.3
1997	241	1121	67.6	1013	89.7
1997	241	1136	68.3	1013	88.1
1997	241	1151	69.8	1013	85.6
1997	241	1206	69.3	1013	85.3
1997	241	1221	69.1	1013	86.6
1997	241	1236	69.8	1013	85.4
1997	241	1251	69.1	1013	85.6
1997	241	1306	69.3	1013	84.8
1997	241	1321	69.5	1013	84.0
1997	241	1336	69.6	1013	82.9
1997	241	1351	69.5	1013	81.7
1997	241	1406	69.9	1013	81.0
1997	241	1421	69.5	1013	80.7
1997	241	1436	70.0	1013	80.8
1997	241	1451	70.2	1013	80.8
1997	241	1506	70.3	1013	80.3
1997	241	1521	70.2	1013	80.1
1997	241	1536	70.1	1013	80.5
1997	241	1551	69.3	1013	80.3
1997	241	1606	68.6	1013	83.1
1997	241	1621	68.2	1013	82.4
1997	241	1636	69.0	1013	80.9
1997	241	1651	68.6	1013	80.2
1997	241	1706	68.4	1013	81.1
1997	241	1721	68.2	1013	81.4
1997	241	1736	68.0	1013	81.0
1997	241	1751	68.0	1013	79.5
1997	241	1806	67.5	1013	80.7
1997	241	1821	67.3	1013	82.1
1997	241	1836	67.1	1012	83.1
1997	241	1851	66.8	1012	84.0
1997	241	1906	66.5	1012	85.2
1997	241	1921	66.1	1012	86.7
1997	241	1936	65.0	1012	88.8
1997	241	1951	63.9	1012	91.6
1997	241	2006	62.8	1012	93.7
1997	241	2021	61.7	1012	95.3
1997	241	2036	60.3	1012	97.6
1997	241	2051	59.4	1012	97.8
1997	241	2106	59.1	1012	97.4

**Phorate Application Meteorological Data (15 min. averages)**

<b>Year</b>	<b>Julian Date</b>	<b>Time</b>	<b>Temp. (F)</b>	<b>Barometric Pressure (hPa)</b>	<b>Relative Humidity</b>
1997	241	2121	58.7	1012	97.3
1997	241	2136	58.4	1012	97.3
1997	241	2151	58.4	1012	97.6
1997	241	2206	57.9	1012	98.3
1997	241	2221	57.7	1012	98.6
1997	241	2236	57.5	1012	98.6
1997	241	2251	57.2	1012	98.4
1997	241	2306	56.9	1012	98.6
1997	241	2321	56.8	1012	98.4
1997	241	2336	56.4	1012	98.7
1997	241	2351	56.1	1012	99.0
1997	242	6	55.9	1012	99.2
1997	242	21	55.9	1012	99.0
1997	242	36	55.8	1012	98.8
1997	242	51	55.4	1012	99.1
1997	242	106	55.3	1012	99.2
1997	242	121	55.2	1012	99.4
1997	242	136	54.9	1012	99.6
1997	242	151	54.7	1012	99.6
1997	242	206	54.5	1012	100.4
1997	242	221	54.5	1012	100.1
1997	242	236	54.3	1012	100.4
1997	242	251	54.3	1012	100.4
1997	242	306	54.2	1012	100.0
1997	242	321	54.0	1011	100.4
1997	242	336	54.0	1011	100.5
1997	242	351	53.9	1011	100.4
1997	242	406	53.8	1011	100.3
1997	242	421	53.8	1011	100.4
1997	242	436	53.8	1011	100.5
1997	242	451	53.8	1011	100.3
1997	242	506	53.8	1011	100.1
1997	242	521	53.8	1011	100.2
1997	242	536	53.6	1011	100.6
1997	242	551	53.6	1011	100.5
1997	242	606	53.6	1011	100.6
1997	242	621	53.5	1011	100.4
1997	242	636	53.5	1011	100.7
1997	242	651	53.5	1011	100.6
1997	242	706	53.7	1011	100.5
1997	242	721	54.4	1011	100.0
1997	242	736	55.9	1011	98.9
1997	242	751	57.0	1011	97.5

**Phorate Application Meteorological Data (15 min. averages)**

<b>Year</b>	<b>Julian Date</b>	<b>Time</b>	<b>Temp. (F)</b>	<b>Barometric Pressure (hPa)</b>	<b>Relative Humidity</b>
1997	242	806	58.2	1011	96.3
1997	242	821	59.6	1011	94.2
1997	242	836	60.8	1011	91.6
1997	242	851	62.5	1011	90.2
1997	242	906	64.8	1011	89.1
1997	242	921	67.2	1011	86.9
1997	242	936	68.8	1011	83.6
1997	242	951	69.1	1011	82.0
1997	242	1006	68.4	1011	82.2
1997	242	1021	69.2	1011	81.4
1997	242	1036	69.0	1011	80.0
1997	242	1051	69.6	1011	78.3
1997	242	1106	69.6	1011	78.1
1997	242	1121	69.3	1011	76.9
1997	242	1136	68.4	1011	78.4
1997	242	1151	67.8	1011	80.8
1997	242	1206	68.4	1011	81.9
1997	242	1221	68.5	1011	81.9
1997	242	1236	68.8	1011	80.5
1997	242	1251	69.1	1011	78.9
1997	242	1306	69.5	1011	77.3